



PII: S0360-1285(97)00015-4

## RECENT TRENDS IN HIGH-ENERGY MATERIALS

J. P. Agrawal†\*

*Physics and Chemistry of Solids, Cavendish Laboratory, University of Cambridge, Cambridge, U.K.*

**Abstract**—A number of new high-energy materials have been reported in the literature in recent years. This review paper examines them under several headings (“thermally stable” or “heat-resistant”, “high-performance”, melt-castable, insensitive, energetic binders, and energetic materials synthesized using  $N_2O_5$ ) and critically examines them from the point of view of stability, reliability, safety and specific application. Problems associated with their processing are identified and suggestions are made to overcome them. © 1998 Elsevier Science Ltd.

**Keywords:** high-energy materials, recent trends, explosive characteristics, advanced explosives, advanced propellants, processing techniques.

### CONTENTS

1. Introduction	1
2. “Heat-resistant” or “Thermally Stable” Explosives	2
2.1. Introduction of Amino Group	2
2.2. Salt Formation	3
2.3. Condensation with a Triazole Ring	3
2.4. Introduction of Conjugation	5
2.5. 3,3'-Diamino-2,2',4,4',6,6'-hexanitrodiphenyl (DIPAM)	5
2.6. $N^2,N^4,N^6$ -tripicrylamine (TPM) or 2,4,6-Tris(picrylamino)-1,3,5-triazine Series of Explosives	5
2.7. Tetranitro Dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)	5
2.8. 2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX)	6
2.9. 2,5-Dipicryl-1,3,4-oxadiazole (DPO)	6
2.10. 2,2',2'',4,4',4'',6,6',6''-Nonanitroterphenyl (NONA)	6
3. High-performance (High VOD) Explosives	7
3.1. Replacement of Nitro Group by Furoxano Group	9
3.2. Introduction of $SF_5$ Groups into Nitro Compounds	11
3.3. Strained and Cage Molecules/Compounds	12
4. Melt-castable Explosives	15
4.1. Tris-X and methyl Tris-X	15
4.2. 1,3,3-Trinitroazetidine (TNAZ)	15
4.3. 4,4'-Dinitro-3,3'-bifurazan (DNBF)	15
5. Energetic Binders for Explosives and Propellants	17
5.1. Polynitropolyphenylenes (PNPs)	17
5.2. Glycidyl Azide Polymer (GAP)	18
5.3. Nitrated HTPB	18
5.4. Poly(NIMMO)	19
5.5. Poly(GLYN)	20
6. Insensitive High Explosives (IHES)	20
6.1. Oxynitrotriazole (ONTA) or Nitrotriazolone (NTO)	21
6.2. Dinitroglycoluril (DINGU)	21
6.3. <i>Trans</i> 1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline (TNAD)	21
7. Energetic Materials Synthesized by Using Nitrogen Pentoxide	23
8. Techniques for Explosive Processing	24
8.1. Melt Casting	24
8.2. Casting	24
8.3. Extrusion	24
8.4. Pressing	24
8.4.1. Direct pressing	25
8.4.2. Incremental pressing	25
8.4.3. Hydrostatic pressing	25
8.4.4. Isostatic pressing	25
9. Conclusions	25
Acknowledgements	25
References	25

### 1. INTRODUCTION

\* Correspondence to Professor J. E. Field, Cavendish Laboratory, Cambridge, U.K.

† On leave from the High Energy Materials Research Laboratory, Pune, India.

Explosives are used for civil as well as military applications. A number of publications which describe their chemistry, synthesis, properties and other salient

features are available in the literature<sup>1-4</sup>. Of course, higher performance has always been a prime requirement in the field of research and development of explosives but, more recently, a combination of properties has become desirable. In addition to a combination of safety, reliability and stability, some specific examples are: heat-resistant explosives for warheads of high-speed missiles and perforation of oil and gas wells, high-performance explosives, insensitive high explosives (IHEs) for low-vulnerability munitions, and melt-castable explosives or explosive binders for better performance. Research is in progress world-wide in order to achieve these goals, and the objective of this review is to give a brief account of such developments during the last decade. Another objective is to examine these explosives critically in the light of their possible applications for specific mission requirements.

The explosives reported in the literature have been classified as follows in order to make the presentation clearer and simpler:

1. "Thermally stable" or "heat-resistant" explosives;
2. High-performance explosives, i.e. high density and high velocity of detonation (VOD) explosives;
3. Melt-castable explosives;
4. Energetic binders for explosive compositions/formulations;
5. Insensitive high explosives (IHEs);
6. Energetic materials synthesized by using nitrogen pentoxide ( $N_2O_5$ ).

## 2. "HEAT-RESISTANT" OR "THERMALLY STABLE" EXPLOSIVES

Explosives with improved high-temperature properties are usually termed as "heat-resistant" or "thermally stable" explosives<sup>5</sup>. The development of space programmes, the drilling of deep oil wells, etc., has resulted in the need for "heat-resistant" or "thermally stable" explosives. This is a new line of research which is being actively pursued world-wide with the aim of producing explosives or explosive compositions that are safe, reliable and stable at high temperatures.

In this area, nitro compounds have received special attention because of their ability to withstand the high temperatures and low pressures encountered in space environments. The research on heat-resistant explosives was reviewed first by Dunstan<sup>6</sup>, followed by Urbanski and Vasudeva<sup>7</sup> and recently by Lu<sup>8</sup>.

From an analysis of the structures of thermally stable explosives, it appears that there are four general approaches to impart thermal stability to explosive molecules:

1. Introduction of amino groups;
2. Condensation with a triazole ring;
3. Salt formation;
4. Introduction of conjugation.

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine or cyclotetramethylene tetranitramine (HMX), with a

melting point of 291°C, is also considered as a heat-resistant explosive in some countries<sup>9,10</sup>, and a safe working limit has been reported as 225°C.

### 2.1. Introduction of Amino Groups

The introduction of an amino ( $-NH_2$ ) group into a benzene ring having a nitro group ( $-NO_2$ ) is one of the simplest approaches to enhance the thermal stability of explosives<sup>11-13</sup>. This is evident from a study of the effect of introducing amino groups in nitrobenzene to form mono-amino-2,4,6-trinitrobenzene (MATB), 1,3-diamino-2,4,6-trinitrobenzene (DATB) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), where the order of thermal stability is  $MATB < TATB$ <sup>14-17</sup>.

DATB and TATB have already qualified as heat-resistant explosives among various nitro derivatives of benzene<sup>18,19</sup>. DATB is fairly stable, with a m.p. of 286°C, but it transforms into a crystalline form of lower density at 216°C, which represents the limit of its utility. The use of DATB in explosive compositions has been described in several patents<sup>20,21</sup>, and it is of practical value in various space applications. On the other hand, TATB has excellent thermal stability in the range 260–290°C, which represents the upper temperature limit at which it may be used. TATB is an explosive with unusual insensitivity and heat resistance, and respectable performance, which places it first on the list of thermally stable and safe explosives. These properties are attributed to several unusual features of the structure of TATB: extremely long C–C bonds in the benzene ring, very short C–N (amino) bonds and six furcated hydrogen bonds. In addition, there is evidence of strong inter- and intramolecular hydrogen bonds in TATB<sup>22</sup>. The net result is that TATB lacks an observable m.p. and has low solubility in all solvents except concentrated  $H_2SO_4$ <sup>23</sup>.

Following the discovery of TATB, it is now preferred to DATB. It is of special interest for the warheads of high-speed guided missiles. By using TATB, energy is sacrificed but handling safety is gained<sup>24,25</sup>. TATB is extensively used in the U.S.A. and a number of pilot plants are available for its manufacture<sup>26</sup>. Polymers such as Estane 5702-F1 and Kel F 800 are considered good binders for TATB. However, the decomposition of Estane binder has cast doubts on the long-term stability of TATB/Estane compositions. TATB/Kel F 800 and TATB/Viton A compositions appear to be attractive for long-term use.

The concept of enhancing thermal stability by the introduction of amino groups is further supported by recent work in China<sup>8</sup> and some typical examples are given in Fig. 1.

These explosives show beyond doubt that the m.p. is raised by the introduction of the amino group. At the same time, the data on thermal decomposition prove that the thermal stability is associated with high melting point and low vapour pressure<sup>27</sup>.

Hexanitrostilbene (HNS) is a heat-resistant explosive with excellent heat resistance that is further improved by the introduction of amino groups<sup>8</sup> (Fig. 2).

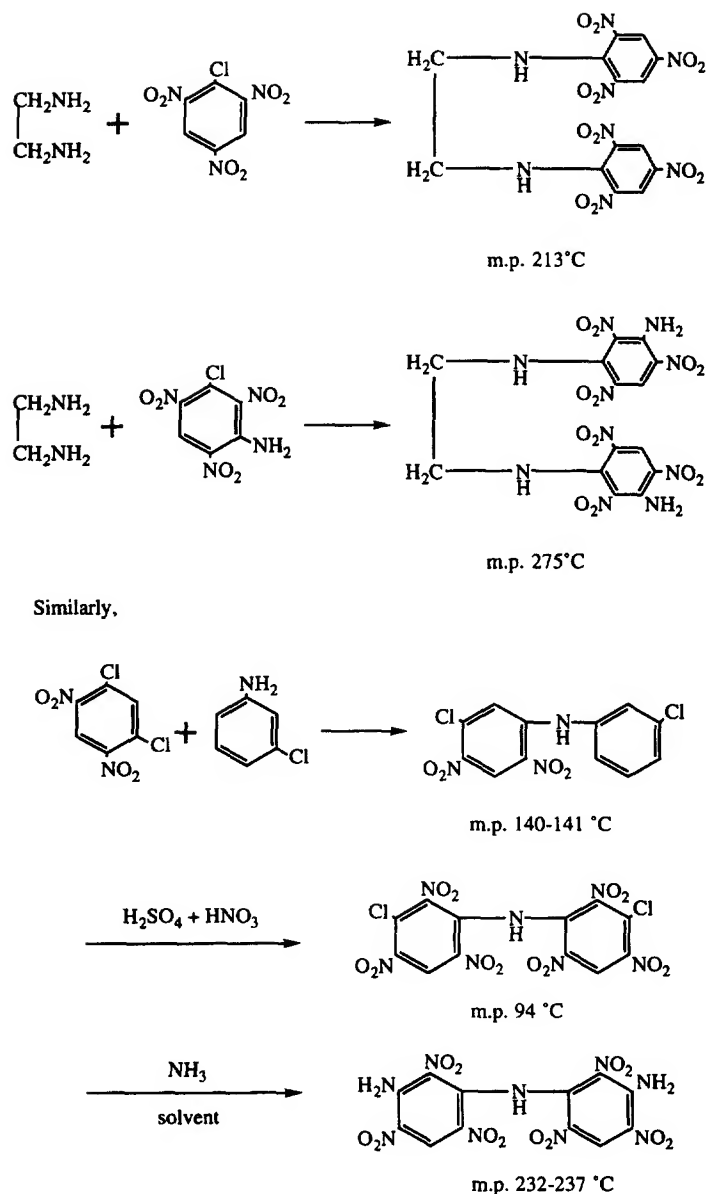


Fig. 1. Caption overleaf.

## 2.2. Salt Formation

Thermal stability is also enhanced by salt formation<sup>28</sup>, which may be illustrated by the example given in Fig. 3.

## 2.3. Condensation with a Triazole Ring

Coburn and Jackson<sup>29</sup> studied in detail the synthesis of various picryl- and picrylamino-substituted 1,2,4-triazoles and 3,3'-bi-1,2,4-triazolyls by condensing the appropriate 1,2,4-triazole or amino-1,2,4-triazole with picryl chloride, and established their structures with infrared (IR) and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopies. On the basis of thermal stability data and impact sensitivity, 3-picrylamino-1,2,4-triazole (PATO) (more thermally stable than the parent compound) was selected.

Its crystal density is 1.94 g cm<sup>-3</sup>, calculated velocity of detonation (VOD) is 7850 m sec<sup>-1</sup>, Chapman-Jouget pressure ( $P_{\text{CJ}}$ ) is 30.7 GPa and impact sensitivity with 2.5 kg weight > 320 cm. It was considered as one of the potentially useful thermally stable explosives. It is relatively inexpensive and is, at the same time, as insensitive as TATB. It was initially thought that it would replace TATB in future applications but its performance is inferior to that of TATB<sup>30</sup>.

PATO has also been synthesized by a Chinese team recently<sup>31</sup> by the condensation of tetryl with 3-amino-1,2,4-triazole, and their data on its thermal stability are in agreement with American work.

PATO is a well-known thermally stable explosive, and Chinese researchers have recently reported its two nitro derivatives<sup>31</sup> with the structures based on IR and NMR

Also,

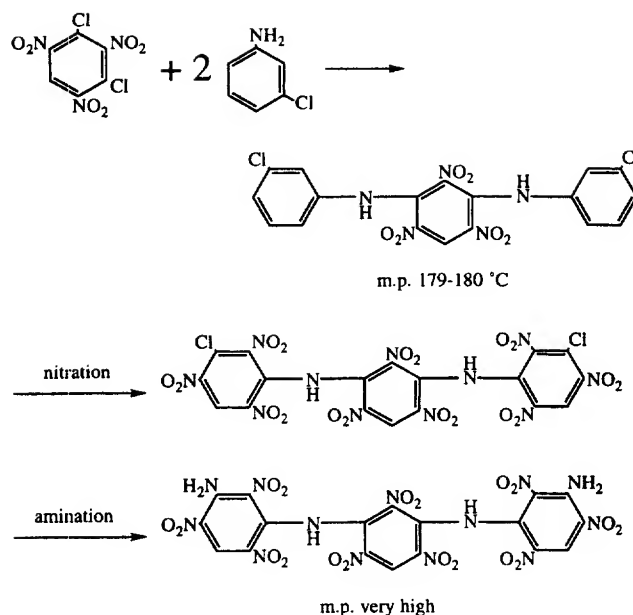


Fig. 1. Effect of introduction of amino groups on thermal stability.

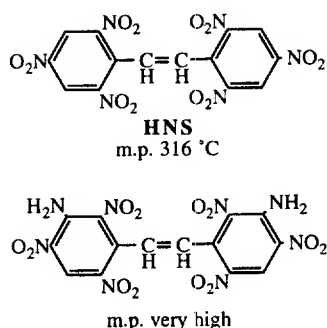


Fig. 2. 5,5'-diamino-2,2',4,4',6,6'-hexanitrostilbene.

(Fig. 4). A comparison of their properties with those of PATO reveals that the thermal stability of these derivatives is not as good as that of the parent compound (PATO). Some experimental and predicted properties of **I** reported by these Chinese investigators are: density

$\approx 1.92 \text{ g cm}^{-3}$ , m.p. *ca.* 103°C, VOD calc.  $\approx 8590 \text{ m sec}^{-1}$  and  $P_{\text{CJ}} \approx 34.5 \text{ GPa}$ . This compound has also been synthesized in the author's laboratory (HEMRL Pune, India), the properties being found to be similar to those reported by the Chinese group. In addition, we have determined impact sensitivity [ $H_{50\%} \approx 28 \text{ cm}$ ]. Being of high density, and high performance (better than RDX), further work is in progress to evaluate its suitability for practical applications.

Similarly, a new compound, styphnyl diaminotriazole (abbreviated as SDATO) and prepared by the condensation of styphnyl chloride with 3-amino-1,2,4-triazole, possesses better thermal stability (Agrawal *et al.* 1995, unpublished work). Its m.p. is  $\approx 320^\circ\text{C}$ , which may be compared with  $310^\circ\text{C}$  for PATO. Exhaustive data indicate that the impact sensitivities of SDATO and PATO are comparable. However, further work is in progress to compare their properties *vis-à-vis* their utility for various applications.

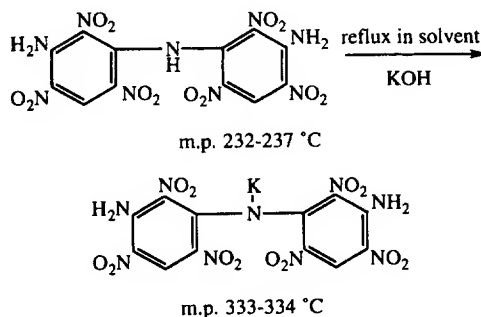


Fig. 3. Potassium salt of 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenyl amine.

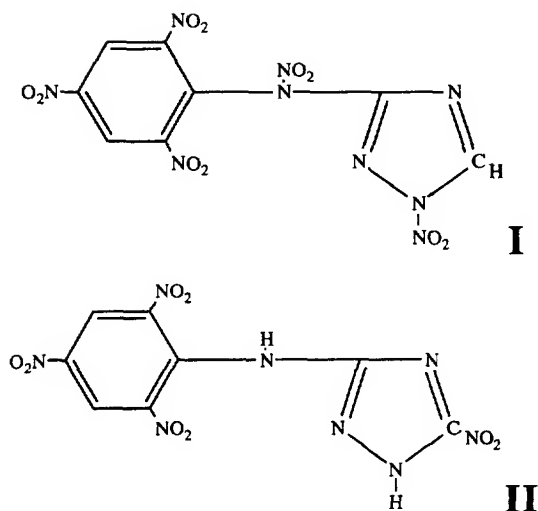


Fig. 4. Nitro derivatives of PATO.

#### 2.4. Introduction of Conjugation

The best example of imparting higher thermal stability through the introduction of conjugation in explosive molecules is hexanitrostilbene (HNS), synthesized by Shipp<sup>32,33</sup> of the American Naval Ordnance Laboratory (NOL) in 1964. Plants for full-scale production exist in the U.K. and China based on the method of Shipp<sup>34</sup>. It proved its efficiency as a heat-resistant explosive as well as a component of heat-resistant compositions employed in the Apollo spaceship and for seismic experiments on the Moon<sup>35</sup>. HNS has also been reported for use in achieving stage separation in space rockets.

Similar to HNS, conjugation exists in hexanitroazobenzene (HNAB) and hexanitrotetrachloroazobenzene (HNTCAB). They are interesting explosives from the point of view of thermal stability<sup>36</sup>. HNAB is of interest because of its m.p. and relative insensitivity compared with pentaerythritol tetranitrate (PETN) and HNS<sup>37</sup>, whereas HNTCAB is a high-temperature-resistant explosive (m.p. ca. 308–314°C) in addition to its likely use as an intermediate for the synthesis of other high-temperature-resistant explosives. It is possible that HNTCAB, on reaction with picramide, DATB, TATB or other amino nitro derivatives, could give birth to a new series of high-temperature-resistant explosives.

In an effort to study the effect of the introduction of  $-C=C-$  on the thermal stability of polynitroaromatics, Feng and Chen<sup>38</sup> designed 3,3'-bis(2,2',4,4',6,6'-hexanitrostilbene) and azo-3,3'-bis(2,2',4,4',6,6'-hexanitrostilbene), synthesized them and studied their structural aspects by IR, NMR, elemental analysis and mass spectrometry. These explosives are expected to have high m.p. and thermal stability in view of their large molecular weights and better molecular symmetry. Further, study of these explosives by differential scanning calorimetry (DSC) also proves that the thermal stability of an explosive is associated with its m.p. Also the decomposition rate is

accelerated when it exists in a molten state. In this series, there is one more explosive, i.e. sym. 2,2',4,4',6,6'-hexanitro-3-methyl nitroaminostilbene, which has also been claimed as a heat-resistant energetic material<sup>39</sup>.

In addition to these heat-resistant explosives, there are some well-known thermally stable explosives which have some additional features. These are described in this section.

#### 2.5. 3,3'-Diamino-2,2',4,4',6,6'-hexanitrodiphenyl (DIPAM)

This is extremely insensitive to electrostatic discharge, requiring more than 32 kJ for initiation. In addition, it has good thermal stability (m.p. ca. 304°C) and has been used to achieve stage separation in space rockets and for seismic experiments on the Moon in a similar manner to HNS<sup>40</sup>.

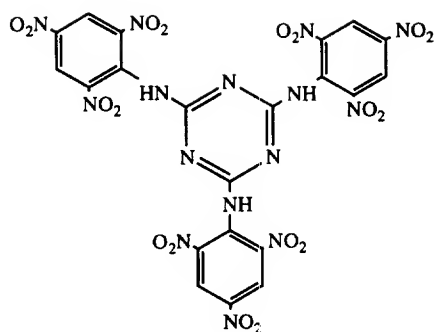
#### 2.6. $N^2,N^4,N^6$ -tripicrylmelamine (TPM) or 2,4,6-tris(picrylamino)-1,3,5-triazine Series of Explosives (Fig. 5)

TPM (I) has been reported to be a moderately thermally stable explosive with performance a little better than that of TNT<sup>41</sup>. Subsequently, the heterocyclic nitrogen atoms of TPM were systematically replaced with the C-nitro function to give nitro-substituted tris(picrylamino) derivatives of pyrimidine (II), pyridine (III) and benzene (IV)<sup>42,43</sup>. The m.p. data show that II is more thermally stable than I. However, the thermal stability decreases with further substitution of C-nitro for heterocyclic nitrogen to give III and IV, in spite of the increased resonance stabilization of the parent ring. The decrease in thermal stability appears to be the result of increased steric crowding about the ring as we proceed from II to IV. This is supported by the fact that when the bulky 4-picrylamino group is removed from III, it yields PYX, one of the most thermally stable explosives reported so far<sup>44</sup>.

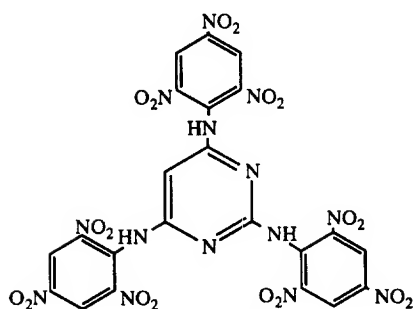
Hercules, Inc., U.S.A. manufactures TPM on a large scale for about the same cost as hexahydro-1,3,5-trinitro-1,3,5-triazine or cyclotrimethylene trinitramine (RDX). China is also reported to have a low-cost, newer manufacturing technology for TPM and has a limited production capability. IV (1,3,5-trinitro-2,4,6-tripicrylaminobenzene) is a readily detonatable, thermally stable secondary explosive synthesized by the reaction of 1,3,5-trichloro-2,4,6-trinitrobenzene (Sym. TCTNB) and picramide in the presence of activated copper powder. Its m.p. is only 234°C but it is still used in booster cup or bridgewire detonators, e.g. for oil-well perforation<sup>45,46</sup>.

#### 2.7. Tetranitro Dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)

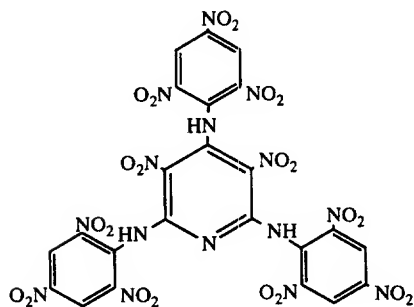
TACOT, a new explosive from Du Pont, is a mixture of isomers with 2-nitro groups substituted in different positions in each benzene ring. As these isomers have



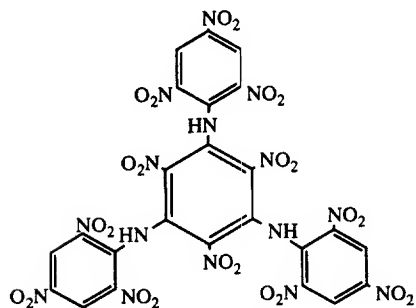
I. m.p. 316°C



II. m.p. 334 °C



III. m.p. 276 °C



IV. m.p. 234 °C

Fig. 5. *N*<sup>2</sup>,*N*<sup>4</sup>,*N*<sup>6</sup>-tripicrylmelamine (TPM) or 2,4,6-tris(picrylamino)-1,3,5-triazine series of explosives.

similar explosive and thermal properties, they are not separated while formulating explosive compositions. It is a powerful explosive with unusual and outstanding high-temperature stability<sup>47-49</sup>. Its ignition temperature (ca. 494°C) is the highest registered for an explosive.

However, its differential thermal analysis (DTA) curve shows that it is stable up to 354°C, after which a slight exothermic reaction starts, which builds into a very rapid deflagration exotherm at 381°C. Its explosive power (VOD of 7250 m sec<sup>-1</sup> at a density of 1.64 g cm<sup>-3</sup>) is equal to 96% that of 2,4,6-trinitrotoluene (TNT) and 80–85% that of RDX. It is highly insensitive to impact and electrostatic charge, but is readily initiated by a lead azide Pb(N<sub>3</sub>)<sub>2</sub> primer with as little as 0.02–0.03 g of Pb(N<sub>3</sub>)<sub>2</sub>. Further, TACOT continues to function effectively even after long exposure to high temperatures. It is available in the form of high-density charges, as a polymer-bonded explosive (PBX) or core lead in explosive cords like Mild Detonating Fuze (MDF) and Flexible Linear Shaped Charge (FLSC). TACOT is also reported to be used to manufacture high-temperature-resistant detonators.

1,3,5,7-Tetranitroadamantane (TNA), with a melting point of ca. 350°C, has also been reported and is likely to be of value as a heat-resistant explosive. Similar to TACOT, it is very insensitive to impact<sup>9</sup>.

#### 2.8. 2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX)

This is produced in high yields from relatively inexpensive starting materials and possesses properties: crystal density 1.75 g cm<sup>-3</sup>, m.p. 460°C, VOD 7450 m sec<sup>-1</sup>, *P*<sub>CJ</sub> 24.2 GPa and impact sensitivity 63 cm. PYX has already been commercialized in America and Chemtronics, Inc. is currently producing it under licence from Los Alamos for use in thermally stable perforators for oil and gas wells<sup>50,51</sup>. It is increasingly being used as a substitute for HNS and is gradually replacing HNS for most commercial, thermally stable explosive applications.

A comparison of the explosive properties of TACOT and PYX indicates that both have comparable thermal stability. However, the former is highly impact-insensitive, whereas the latter is slightly impact-sensitive. Quality control of PYX during manufacture is much easier than for TACOT as PYX is a pure compound whereas TACOT consists of a mixture of several isomers.

#### 2.9. 2,5-Dipicryl-1,3,4-oxadiazole (DPO)

The renewed interest in thermally stable but shock-sensitive explosives for use in detonation-transferring compositions has given birth to DPO<sup>52</sup>. DPO possesses a unique combination of impact sensitivity (*H*<sub>50%</sub> = 20 cm) and thermal stability. According to Sitzmann, its high impact sensitivity is attributed to the N–N bond of the oxadiazole ring, which provides a trigger linkage<sup>53</sup>. DPO is generally considered as a thermally stable substitute for PETN.

#### 2.10. 2,2',2'',4,4',4'',6,6',6''-Nonanitroterphenyl (NONA)

This is produced by the condensation of 2 moles of picryl chloride with 1,3-dichloro-2,4,6-trinitrobenzene

in the presence of copper dust at 210°C and nitrobenzene as a medium<sup>54</sup> (Ullmann condensation). It has a density of 1.78 g cm<sup>-3</sup> and exceptional heat stability, melting at 440–450°C with decomposition, which together with a low volume of split-off gases render it an interesting material for booster explosives in space technology<sup>55</sup>.

Another potential heat-resistant explosive is a polynitro derivative of 2,5,8-triphenyl-tris(triazolobenzene), obtained by the coupling reaction of the diazotized nitroanilines with 1,3,5-triaminobenzene followed by oxidation with CuSO<sub>4</sub>. The product obtained with *p*-nitroaminobenzene has an m.p. of 370°C whereas that obtained with 2,4-dinitroaminobenzene has an m.p. of 400°C.

Large-ring polynitro compounds are important heat-resistant explosives and, accordingly, large-ring octanitro explosive has been reported to possess excellent heat-resistant efficiency<sup>56</sup>. The compound synthesized by *m*-dichlorobenzene and resorcinol as the starting materials has a m.p. of ca. 350°C.

Ritter and co-workers have recently reported a new class of explosives known as polynitropyridines: 2,4,6-trinitropyridine oxide (I), 2,4,6-trinitropyridine (II) and 2,6-diazo-4-nitropyridine-1-oxide (III), and characterized them by spectroscopic and thermoanalytical methods. II has a heat-resistance comparable to that of TNB and an impact-sensitivity comparable to that of RDX. These are high explosives with performance superior to sym. trinitrobenzene (TNB) and TNT<sup>57</sup>.

Buckley and co-workers have done pioneering work on the synthesis of new heat-resistant explosives from

naphthalene. They have synthesized tetranitro derivatives, with markedly high melting points, from 2,4-dimethyl-1,5-dinitronaphthalene using HNO<sub>3</sub> in acetic anhydride. The trinitro compound is also present as an impurity in these nitro derivatives<sup>58,59</sup>.

The effect of various radiations, such as gamma radiation from <sup>60</sup>Co, on some heat-resistant explosives such as DATB, TATB and TACOT has also been studied by Avrami, the data indicating that these explosives are remarkably stable<sup>60</sup>.

The material in this section is summarized in Table 1.

### 3. HIGH-PERFORMANCE (HIGH VOD) EXPLOSIVES

It has always been an aim of explosive technologists to achieve higher performance for warhead applications. An increase in density improves the performance without increasing the sensitivity as the detonation pressure,  $P_{CJ}$ , is proportional to the density<sup>68–70</sup> or

$$P_{CJ} = \frac{\rho D^2}{4} \quad (1)$$

where  $P_{CJ}$  is measured in Pascals,  $\rho$  is the density of the composition in g cm<sup>-3</sup>, and  $D$  is the VOD in m sec<sup>-1</sup>. Clearly, high detonation velocities lead to high performance as well.

On the other hand, an increase in oxygen balance (OB) and heat of formation generally increases the sensitivity of an explosive as well as its performance<sup>71</sup>. The recently developed crystal-density predictive methods have been

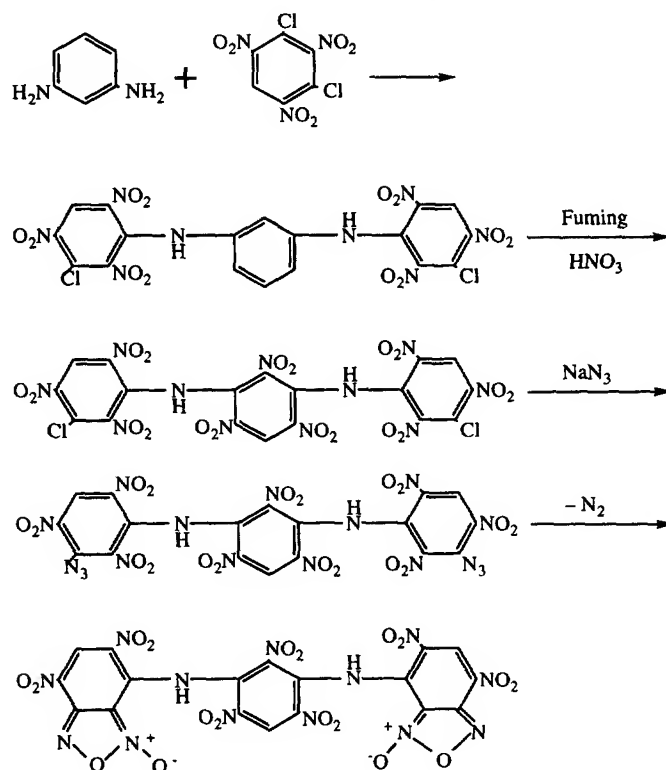


Fig. 6. Effect of replacement of nitro group by furoxano group on performance.

Table 1. Some properties of "heat-resistant" or "thermally stable" explosives. A comparison of the impact sensitivity of these explosives (reported by various teams from different laboratories) would not be correct as sometimes the data are not reproducible even when using the same Impact Sensitivity Tester under the same conditions by the same skilled operator. Thus the data obtained from a range of testers only give a crude relative ranking of the impact sensitivity of these energetic materials<sup>61-67</sup>.

Name	Structure/formula	Melting point /°C	Density g/ml	Impact* sensitivity/ cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
1,3-diamino-2,4,6-trinitrobenzene (DATB)		286	1.84		7,500	Space applications
1,3,5-triamino-2,4,6-trinitrobenzene (TATB)		350	1.94	Insensitive	8,000	Explosive with unusual insensitivity and heat resistance.
2,2',4,4',6,6'-hexanitrostilbene (HNS)		316	1.74		7,000	Employed for Apollo spaceship and seismic expts. on the Moon
5,5'-diamino-2,2',4,4',6,6'-hexanitrostilbene (DAHNS)		very high				
3-picrylamino-1,2,4-triazole (PATO)		310	1.94	>320	7850	A potential replacement for TATB but performance poorer than TATB
2,4-bis (3-amino 2,4-triazole) 1,3,5-trinitrobenzene (SDATO)		320	1.96	165-170	cal. 7600	
2,2',4,4',6,6'-hexa-nitroazo benzene (HNAB)		220				Relatively insensitive compared to PETN and HNS
2,2',4,4',6,6'-hexanitro-3,3',5,5'-tetrachloroazo-benzene (HNTCAB)		308-314				Intermediate for synthesis of other heat-resistant explosives
3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenyl (DIPAM)		304	1.79			Used for stage separation in rockets



Table 1. —continued

Name	Structure/formula	Melting point /°C	Density g/ml	Impact* sensitivity/ cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
1,3,5-trinitro-2,4,6-tripicryl-aminobenzene		234				Readily detonable, thermally stable secondary explosive
2,6-bis(picryl-amino)-3,5-dinitropyridine (PYX)		460	1.75	63	7450	Thermally stable perforators for oil and gas wells. A substitute for HNS
Tetranitro-dibenzo-1,3a,4,4a-tetraazapentalene (TACOT)		494 (ignition)	1.85	very insensitive	7250	Stable up to 354 °C. Used for Flexible Linear Shaped Charge and high-temperature resistant detonators
2,5-dipicryl-1,3,4-oxadiazole (DPO)			1.77	20		Used for detonation transferring compositions
N <sup>2</sup> ,N <sup>4</sup> ,N <sup>6</sup> -tripicrylamino melamine (TPM)		316				Thermally stable explosive with a little better performance than TNT
2,2',2'',4,4',4'',6,6'6''-nonanitro-terphenyl (NONA)		440-450	1.78			Decomposes on melting. Of interest for booster explosives in space technology

very valuable in directing research efforts towards high-density explosives. These methods predict unusually high densities for two general classes of compound—hydrogen-free nitro heterocycles and polynitro cage compounds.

There are three general approaches to enhance density and thus performance of explosives:

1. Replacement of nitro group by furoxano group;

2. Introduction of pentafluorosulfonyl (SF<sub>5</sub>) group into nitro compounds;
3. Formation of cage-like structures.

### 3.1. Replacement of Nitro Group by Furoxano Group

A new area of interest and activity in recent years has

been the development of new explosives with increased performance coupled with increased stability and insensitivity<sup>72</sup>. In order to meet these requirements, several Chinese investigators have reported that the replacement of the  $-\text{NO}_2$  group by a furoxano group results in an increase in density and detonation velocity<sup>73</sup>. The introduction of  $-\text{NH}_2$  groups in explosive molecules is reported to increase densities in addition to heat resistance, as discussed earlier. By exploiting this concept, one such explosive, *N,N'*-bis(2,4-dinitrobenzofuroxan)-1,3,5-trinitro-2,6-diaminobenzene, has been prepared by the scheme<sup>74</sup> given in Fig. 6. This compound possesses a density of  $1.92 \text{ g cm}^{-3}$

and  $\text{VOD} \approx 8570 \text{ m sec}^{-1}$  with no loss of weight at  $100^\circ\text{C}$  for 48 hr. The density of this explosive is higher than those of PYX<sup>75</sup> and 2,4,6-tris(picrylamino)-1,3,5-triazine<sup>41</sup>. Furthermore, the cost of production is likely to be low because of the inexpensive starting materials.

Another interesting explosive in this class is 5,7-diamino-4,6-dinitrobenzofuroxan<sup>76</sup> which is synthesized by the scheme shown in Fig. 7. The authors have claimed that the density of this explosive is high ( $1.91 \text{ g cm}^{-3}$ ), that it is more powerful ( $\text{VOD} \approx 8050 \text{ m sec}^{-1}$ ) than TATB ( $\text{VOD} \approx 8000 \text{ m sec}^{-1}$ ) and, at the same time, that it is insensitive<sup>77</sup>. A comparison with TATB and DADNBF shows that it lies between these two

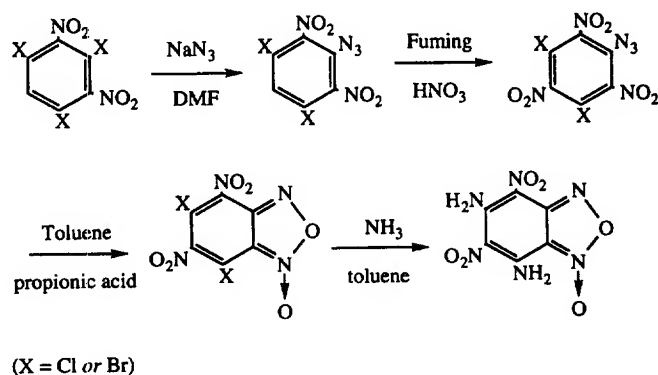


Fig. 7. Synthesis scheme of DADNBF.

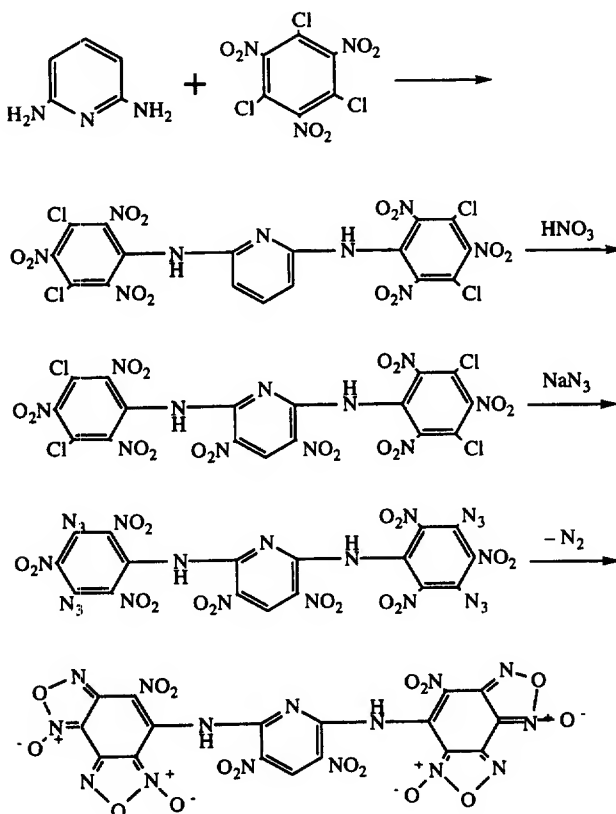


Fig. 8. Effect of introduction of pyridine and amino groups on density, heat resistance and impact sensitivity.

explosives with respect to density and VOD. Similarly, the introduction of pyridine in addition to an  $-NH_2$  group further increases density, heat resistance and decreases impact sensitivity. Accordingly, the explosive *N, N'*-bis(2-nitrobenzodifuroxanyl)-3,5-dinitro-2,6-diaminopyridine (Fig. 8) has been designed, synthesized and characterized by elemental analysis, IR,  $^1H$ -NMR and mass spectrometry and studied for explosive properties (density  $\approx 1.91 \text{ g cm}^{-3}$ , calc. VOD  $\approx 8630 \text{ m sec}^{-1}$  and m.p. ca.  $231^\circ\text{C}$ )<sup>78</sup>. This explosive is better than PYX with respect to density as well as VOD, and the yield is also reported to be higher.

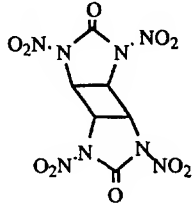
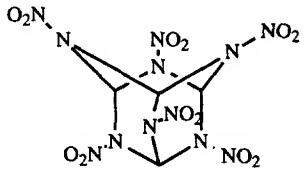
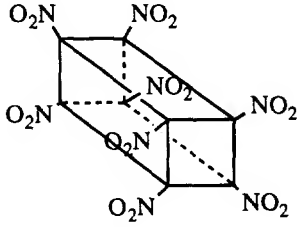
Wang and co-workers<sup>79</sup> have also reviewed research on benzofuroxan-based explosives and reported a high-energy and low-sensitivity explosive *N,N',N''*-tris(2-nitrobenzodifuroxanyl)melamine. The data on its explosive properties (density  $\approx 1.90 \text{ g cm}^{-3}$ , calc. VOD  $\approx 8695 \text{ m sec}^{-1}$  and m.p. ca.  $316^\circ\text{C}$ ) show that it is a high-performance as well as a thermally stable explosive.

It is evident that amino substitution may be regarded as a way of enhancing the melting point (thermal stability) as well as the density of nitro aromatic compounds. This is attributed to its ability to undergo strong hydrogen bonding with neighbouring nitro groups and its ability to strengthen the  $-C-NO_2$  bond of an *ortho* or *para* nitro group. At the same time, it decreases the impact sensitivity<sup>80</sup>.

### 3.2. Introduction of $SF_5$ Groups into Nitro Compounds

As a part of continuing research for energetic materials that combine high performance with low vulnerability towards accidental detonation, the effect of the pentafluorosulfonyl ( $SF_5$ ) group on the properties of explosive nitro compounds has recently been reported<sup>81</sup>. This is based on the fact that more energy is released due to the formation of HF in the detonation of  $SF_5$  explosives ( $S-F$  bond energy =  $79 \text{ kcal mol}^{-1}$ , that of  $H-F$  =  $136 \text{ kcal mol}^{-1}$ , whereas the  $Al-F$  bond energy is  $158 \text{ kcal mol}^{-1}$ ). It is also well established that the substitution of H by F in hydrocarbons leads to a significant increase in density<sup>82</sup>. This implies that the  $SF_5$  group would provide nitro explosives with higher density or, in other words, improved performance<sup>83</sup>. On the basis of these assumptions, some polynitro  $SF_5$  explosives have been designed and their performance predicted; the performance is in agreement with the predictions. The initial experiments of Sitzmann *et al.* support the hypothesis that the  $SF_5$  group can provide explosives with improved properties: increased density, decreased sensitivity and higher energy coupled with better thermal stability—a unique combination of properties. This work was begun only recently in America and it may take a few more years before nitro explosives with  $SF_5$  groups come out of the laboratories.

Table 2. Explosive characteristics of some cage compounds

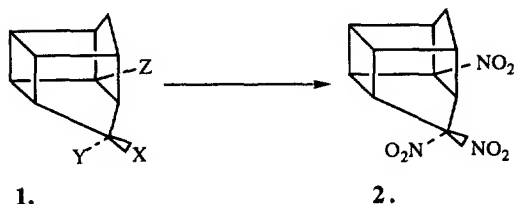
Compound	Structure	Density g/ml	VOD m/s	Detonation Pressure/ GPa
Tetraaza-nitroglycurilo cyclobutane		1.99	8400	33
Hexaaza-nitro adamantane		2.10	9500	43.5
Octanitro Cubane		2.00	9800	46.7

### 3.3. Strained and Cage Molecules/Compounds

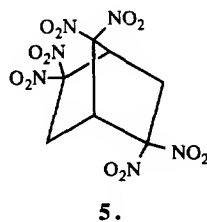
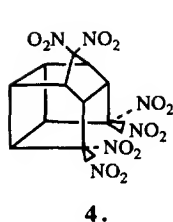
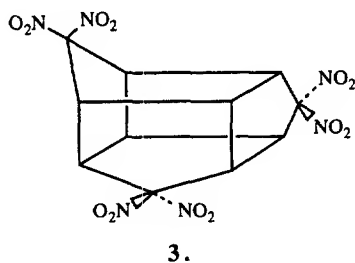
Energetic materials of the strained-ring and cage families may constitute a promising new class of explosives. This was based on the fact that the compounds of this family have high strain energies locked in the molecules (steric strain is expressed as increased positive heat of formation as compared with a corresponding unstrained system and is released as extra energy on detonation). They also possess rigid and highly compact structures, resulting in increased density. Thus greater mass of polynitro polycyclic strained and cage compounds may be accommodated in a given volume which, along with their high molecular strain energies, results in a better performance on detonation.

Considerable current interest and sustained research efforts of some groups in the U.S.A. have been aimed at the chemistry and synthesis of strained energetic compounds. According to Marchand, polynitro polycyclic cage compounds are important members of this class<sup>84</sup>.

The general approach of Marchand and his team<sup>85</sup> is to construct appropriately substituted cage molecules (where X, Y are carbonyl oxygen and Z is  $-\text{COOH}$ ) and subsequently convert the substituents (X, Y and Z) into  $\text{C}-\text{NO}_2$  groups as shown below.



This approach has been successful for the synthesis of several polynitro polycyclic cage compounds. Some representative examples are shown below (compounds 2-5)<sup>86-89</sup>.



Another line of research in the field of cage compounds concerns the synthesis of pentacyclo-[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonane-2,4-bis(trinitroethylester), which possesses a low m.p. and high thermal stability. It is a potential energetic plasticizer for explosives/propellants<sup>90</sup>. Chinese researchers have synthesized this plasticizer starting with hydroquinone (a readily available and inexpensive starting material) via bromination, oxidation, Diels-Alder reaction with pentacyclodine, (2 + 2) photocyclization and Favorskii rearrangement to yield homocubane dicarboxylic acid, which is first converted into diacid chlorides followed by condensation with trinitroethanol. The scheme is given in Fig. 9.

ARDEC has also made significant contributions in this field and synthesized a number of cage compounds with an optimum number of nitro groups which are more powerful than HMX. This is attributed to their high crystal densities combined with the high strain energies of cage systems<sup>91</sup>. The synthesis of 1,4-dinitrocubane has also been reported through various routes by other groups<sup>92,93</sup>. Some important compounds reported in this field, along with their predicted explosive characteristics, are given in Table 2.

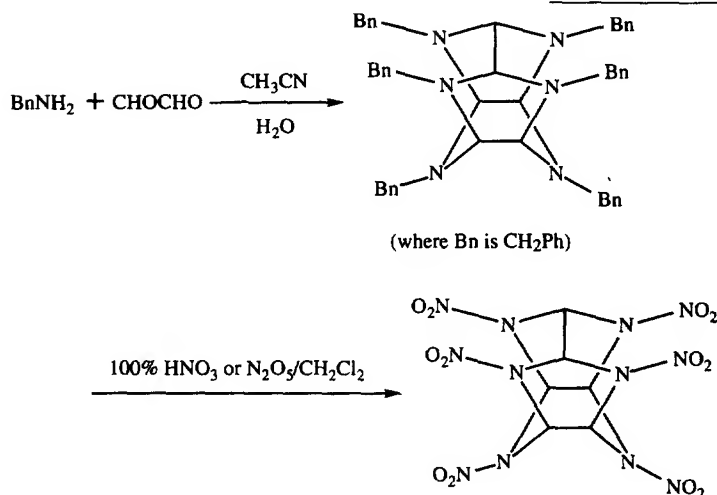
A study of the nitro derivatives of seven varieties of carbocyclic cage compounds, including (in descending order of molecular strain) cubane, bishomocubane, bishomopentaprismane and adamantane, reveals that, while cubane derivatives in general are thermally stable, bishomocubane and adamantane derivatives are even more stable as expected owing to the reduced cage strain in these molecules. With the use of the Kamlet-Jacobs Simple Method, the theoretical number of nitro groups required for maximum detonation performance of carbocyclic cage structures has also been predicted, and is shown in Table 3.

The multi-nitrated caged explosive (3,7,9-trinitronor-adamantane), which is highly strained, has been reported by Zajac and claimed to be highly energetic<sup>94</sup>. Cubane has also been reported as a binder for propellants (cubane/AP/Al and cubane/HAP/Al) which are reported to have a very high specific impulse<sup>95</sup>. Ionic salts of cage molecules—adamantyl tetrakis(ammonium nitrate), adamantyl and cubyl poly(ammonium nitroformate)s—are high-density, energetic and water-soluble. They appear to be attractive in new hydroxyl ammonium nitrate (HAN) based liquid gun-propellant formulations and are currently being investigated for such applications<sup>96</sup>.

The preliminary evaluation of polynitro polycyclic cage compounds for their explosive performance characteristics indicates that this class of explosives is both relatively powerful and shock-insensitive. As a result, it is thought that polynitro polycyclic cage compounds may be valuable for use as explosive/propellant ingredients in military applications in the near future.

Extensive research on cage compounds has resulted in the discovery of hexanitrohexaazaisowurtzitane (HNIW, popularly known as CL-20). It is the most celebrated product of many years of research at the Naval Air

Warfare Center (NAWC) by Neilson and co-workers on the synthesis of novel nitramines and related energetic materials<sup>97,98</sup>. It exists in five polymorphic forms:  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  (not fully established) and  $\epsilon$ . The  $\epsilon$  form is the most suitable as a high-performance explosive. The first member of the hexaazaisowurtzitane family is the hexabenzyl derivative (HBIW) which is further elaborated to HNIW by the following scheme:



The Thiokol Corporation, U.S.A., has modified the original route discovered by Neilson and scaled-up to pilot scale<sup>99</sup>. Some of the properties of CL-20 are: density 2.04 g cm<sup>-3</sup>, VOD 9380 m sec<sup>-1</sup> and DSC decomposition temperature 228°C. It is reported to be compatible with nitramines, nitrate esters, azidopolymers, poly(ethylene glycol) (PEG), hydroxy-terminated polybutadiene (HTPB), ammonium perchlorate (AP), ammonium nitrate (AN), etc., and has potential as a high-performance explosive as well as an ingredient of propellant formulations.

In addition to these approaches for the synthesis of high-performance explosives, there are other explosives

reported in the literature that are worth mentioning. These are nitramines with bisimidazolidine-dione backbone include 1,4-dinitrotyrosyl (DINGU) and 1,3,4,6-tetranitrotyrosyl (TNGU or Sorguyl, French). TNGU is categorized as a high-performance explosive, for which DINGU is the starting material. DINGU, on nitration with a nitrating mixture consisting of 80% HNO<sub>3</sub> and 20% (0.38 mol) of N<sub>2</sub>O<sub>5</sub>, gives TNGU which

has a density of 1.94 g cm<sup>-3</sup>, VOD of 9070 m sec<sup>-1</sup>, a decomposition temperature of ca. 200°C and is stable up to 100°C. The VOD and brisance are superior to those of HMX. TNGU is, however, readily decomposed by water and polar solvents even at a temperature of 10–15°C<sup>100</sup>. Its thermal decomposition has also been reported by Oyumi and Brill<sup>101</sup>.

Another interesting explosive reported recently is tetranitropropanediurea, with a density of 1.98 g cm<sup>-3</sup> and good thermal stability. It is synthesized by the nitration of propane diurea (a condensation product of 1,1,3,3-tetraethoxypropane with urea in an acidic medium), with HNO<sub>3</sub>–(CH<sub>3</sub>CO)<sub>2</sub>O nitrating agent. Its

Table 3. Predicted properties of carbocyclic cage compounds

Parent hydrocarbon cage compound	Composition of polynitro cage			$\rho$ (g cm <sup>-3</sup> )	$\Delta H_f^0$ (kcal mol <sup>-1</sup> )	Molecular strain energy (kcal mol <sup>-1</sup> )	Av. C–C strain energy (kcal mol <sup>-1</sup> )	$P_{CJ}$ (GPa)
	C	N	NO <sub>2</sub>					
Tetrahedrane	4	0	4	2.138	88.03	126	21.0	51.2
Triprismane	6	0	6	2.138	80.03	137	15.2	49.3
Cubane	8	0	8	2.098	81.04	157	13.1	46.7
Homocubane	9	1	9	2.094	30.08	122	9.4	45.3
1,3-Bishomocubane	10	1	11	2.092	– 33.83	82.6	5.9	43.1
Bishomopentaprismane	12	2	12	2.057	– 56.76	70.1	4.1	42.1
Trishomocubane	11	2	12	2.063	– 75.3	57.1	3.8	41.9
Diamantane	14	5	15	2.048	– 170.47	9.8	0.5	41.5
Adamantane	10	5	11	1.959	– 136.69	5.6	0.5	38.3
HMX <sup>†</sup>	4 <sup>‡</sup>	8	4	1.903	17.4	0	0	38.2

<sup>\*</sup>Modified by taking cubane as basis for calculation.

<sup>†</sup>Included for comparison.

<sup>‡</sup>The two-dimensional ring contains four nitrogen atoms in addition.

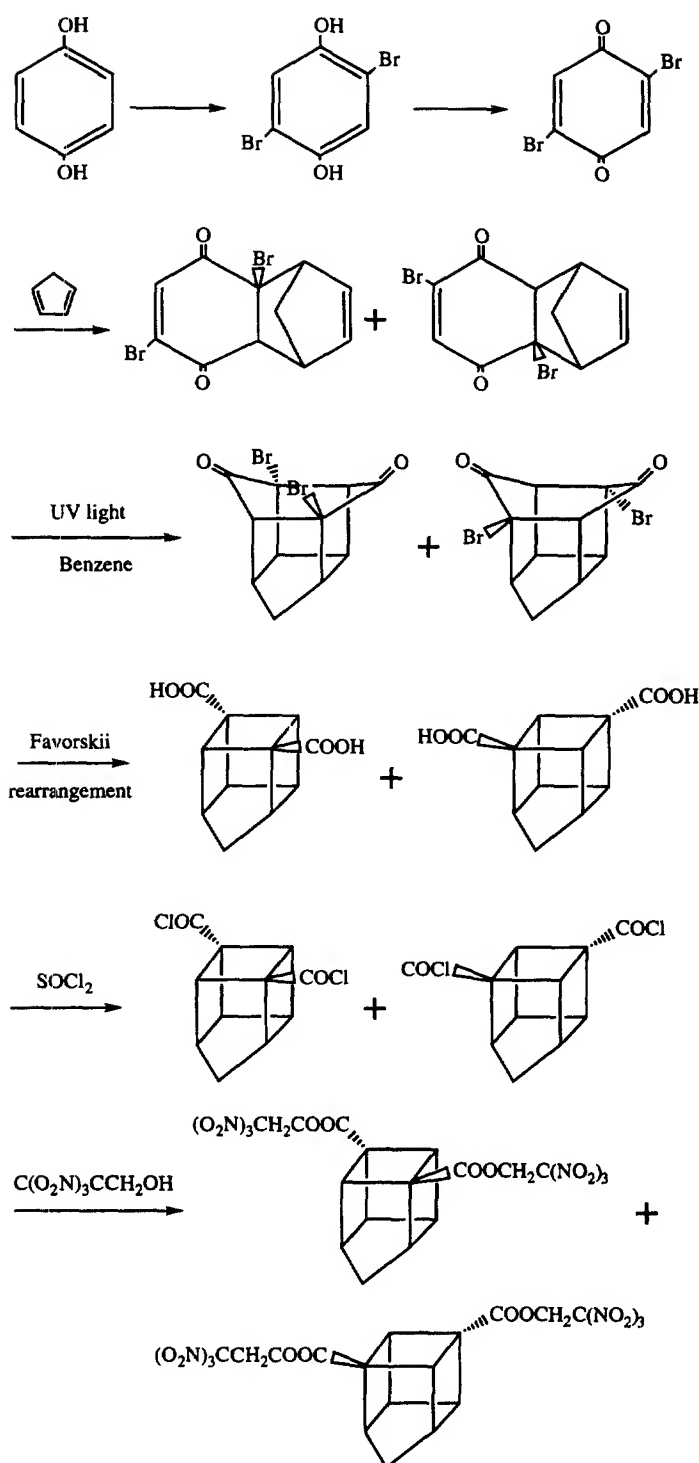


Fig. 9. Synthesis scheme of a cage plasticizer.

explosive properties indicate that it is superior to TNGU and has potential in a variety of applications. However, it needs more evaluation to establish its superiority<sup>102</sup>.

French researchers have recently reported a new explosive called 1,3,5,5-tetranitrohexahydropyrimidine (DNNC), which may also find application as an oxidant for propellant and pyrotechnic formulations<sup>103</sup>. It was

first synthesized in 1982<sup>104</sup> and has the following properties: m.p. 151–154°C, density  $\approx 1.82 \text{ g cm}^{-3}$ , VOD of 8730 m sec<sup>-1</sup> and  $P_{\text{CI}} \approx 34 \text{ GPa}$ . The opinion of American researchers is that it is an excellent oxidant (OB  $\approx 6\%$ ) with very low impact sensitivity and may be used as an oxidizer for explosive/pyrotechnic/rocket propellant compositions<sup>105</sup>.

DNNC's six-membered ring is a unique heterocyclic molecule which combines chemical structural features found separately in energetic geminal dinitroalkane compounds and cyclic RDX nitramine. This hybrid molecular structure of DNNC produces an energetic compound with an impact initiation sensitivity much lower than that of RDX and more like that exhibited by TNT. In the opinion of Shackelford and Goldman, DNNC is an inherently thermally stable and insensitive high-energy oxidizer that could be a potential replacement candidate for cyclic six-membered RDX nitramine<sup>106</sup>.

Because of their favourable elemental composition, heteroaromatic nitro compounds represent explosives of high performance (oxygen balance, density, heat of formation and VOD) as compared with analogous aromatic explosives<sup>107–109</sup>. With this objective, Licht and co-workers have synthesized some methylnitramine-substituted pyridines and triazines, established their structures, and characterized them for thermal and impact sensitivities. The data on impact sensitivity, however, indicate that tetryl may not be replaced by these explosives<sup>110</sup>.

Some explosives based on naphthalene with high energy and high density have also been suggested in the literature. 2,6-Diamino-1,4,5,8-tetranitronaphthalene is a potential explosive with the following properties: density  $\approx 1.78 \text{ g cm}^{-3}$ , OB  $\approx 71.0\%$ , calc. VOD  $\approx 7000 \text{ m sec}^{-1}$  and impact sensitivity ( $H_{50\%}$ )  $\approx 35\text{--}27 \text{ cm}$  with a 2.5 kg, type 12 tool. However, its synthesis is complex and involves six steps starting with 2,6-dimethylnaphthalene<sup>111</sup>.

The most powerful explosive reported so far is HHTDD [2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatricyclo(7,3,0,0)dodecane-5,11-dione] with an oxygen balance  $\approx 0$ , crystal density  $\approx 2.07 \text{ g cm}^{-3}$  and estimated VOD  $\approx 9700 \text{ m sec}^{-1}$ . Such properties support the claim of the Chinese researchers Hu and co-workers (unpublished research, 1992). However, it may not find any application, because water and acidity affect its stability. Its thermal decomposition has also been reported recently<sup>112</sup>.

While reviewing the work at the Los Alamos National Laboratory, U.S.A., Coburn *et al.*<sup>113</sup> have predicted the synthesis and performance of a number of explosives, such as 2,4,6-trinitro-1,3,5-triazine (crystal density  $\approx 1.98 \text{ g cm}^{-3}$  and VOD  $\approx 9280 \text{ m sec}^{-1}$ ), 3,6-dinitro-1,2,4,5-tetrazine and dinitrofuran (DNF), but their efforts to synthesize them through several routes have not been successful.

The material in this section is summarized in Table 4.

In order to increase the performance level of conventional warheads, it is necessary to increase the energy output of the explosives that are used for their filling. In plastic-bonded explosives (PBXs), a polymer binds the crystals of explosive thus imparting mechanical integrity to the explosive charge and, at the same time, helping ensure safety during handling. However, the use of inert polymers brings down the energy of the system. There are generally two approaches for maintaining the same energy level or enhancing the energy of

the system involving the use of melt-castable explosives and/or energetic binders.

#### 4. MELT-CASTABLE EXPLOSIVES

Such explosives, except for TNT, are of recent origin and only a few explosives have recently been reported for such applications.

##### 4.1. *Tris-X and Methyl Tris-X*

Millar *et al.*<sup>114</sup> have synthesized two heterocyclic trinitramines (Tris-X and its homologue "Methyl Tris-X"), established their structures by elemental analysis, IR, NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) and mass spectrometry and studied "Tris-X" for explosive properties (crystal density  $1.73 \text{ g cm}^{-3}$ , calc.  $P_{\text{CJ}} \approx 30 \text{ GPa}$ , calc. VOD  $\approx 8700 \text{ m sec}^{-1}$ , Figure of Insensitiveness (F of I)  $\approx 57$  (on a scale where RDX has an F of I = 60) and m.p. ca.  $68\text{--}69^\circ\text{C}$ ). These can be easily synthesized in large yields by using  $\text{N}_2\text{O}_5$  technology. The low m.p. indicates its suitability as a melt-castable explosive using steam processing. However, its thermal stability (by DSC and chemiluminescence) is only marginally acceptable, suggesting that this family of explosives is unlikely to be used for munitions.

##### 4.2. *1,3,3-Trinitroazetidine (TNAZ)*

Another potential explosive in this class is 1,3,3-trinitroazetidine (TNAZ) reported by Iyer and his team<sup>96</sup>. This is a new strained-ring energetic material with an m.p. of  $101^\circ\text{C}$ , density ( $d_{\text{X-ray}}$ ) of  $1.84 \text{ g cm}^{-3}$ <sup>115</sup> and thermal stability of over  $240^\circ\text{C}$ <sup>116</sup>. Similar to "Tris-X", it is also a melt-castable explosive and may be processed with steam. Further, it has many added advantages over known explosives. Unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminium, steel, brass and glass. Also, it is not hygroscopic and does not pose problems from a processing viewpoint. It provides up to 10% increased energy relative to RDX in the low-vulnerability ammunition (LOVA) XM-39 gun-propellant formulations<sup>117</sup>. A comparison of the energetics in XM-39 type formulations is: RDX  $1069 \text{ J g}^{-1}$ , HMX  $1063 \text{ J g}^{-1}$  and TNAZ  $1160 \text{ J g}^{-1}$ . On the basis of these properties, it may safely be concluded that TNAZ is a steam-castable material which is attractive as an explosive or as a near-term candidate component for explosives/propellants with low sensitivity, good stability and enhanced performance (high energy and density) over existing military formulations.

##### 4.3. *4,4'-Dinitro-3,3'-bifurazan (DNBF)*

DNBF has been reported by Coburn<sup>118,119</sup> as having the following properties: melting point  $85^\circ\text{C}$ , thermal stability (DTA)  $254^\circ\text{C}$ , impact sensitivity  $12 \text{ cm}$ , calc. crystal density  $1.92 \text{ g cm}^{-3}$ , VOD  $8800 \text{ m sec}^{-1}$  and  $P_{\text{CJ}}$

Table 4. Properties of some high-performance explosives

Name	Structure/formula	Melting point /°C	Density g/ml	Impact sensitivity/ cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
N,N'-bis(2,4-dinitro benzofuroxan)-1,3,5-trinitro-2,6-diamino benzene			1.92		8570	
N,N'-bis(2-nitro-benzodifuroxanyl)-3,5-dinitro-2,6-diamino pyridine		231	1.91		8630	Better than PYX with respect to density and VOD
5,7-diamino-4,6-dinitro benzofuroxan			1.91	Insensitive	8050	
N,N',N''-tris(2-nitro benzo-difuroxanyl) melamine		316	1.90		8695	Higher performance as well as thermally stable
1,3,4,6 tetra-nitro glycoluril (TNGU or Sorguyl)			1.94		9070	It is readily decomposed by water and other polar solvents
Tetranitro-propane diurea			1.98	H <sub>100%</sub> =25 (10 kg weight)	9030	Preparation is easy. Good thermal stability, and superior to TNGU
1,3,5,5-tetra-nitro hexa-hydro pyrimidine (DNNC)		151-4	1.82	Insensitive	8730	Excellent oxidant for explosive, propellant and pyrotechnic compositions



Table 4. —(continued)

Name	Structure/formula	Melting point /°C	Density g/ml	Impact sensitivity/cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
2,6-diamino-1,4,5,8 tetra-nitro naphthalene			1.78	H <sub>50</sub> %≈35	7000	Synthesis involves six steps
2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatri-cyclo[7.3.0.0.] dodecane-5,11-dione (HHTDD)			2.07		9700	Water and acidity affect stability adversely

35.6 GPa. The low m.p. and predicted high performance make DNBf a very attractive melt-castable explosive. It is, however, very sensitive to impact, demanding stringent safety measures during synthesis and handling.

As pointed out earlier, the introduction of SF<sub>5</sub> groups has a strong tendency to lower the melting points of nitro explosives. Therefore, introduction of SF<sub>5</sub> groups into nitro explosives may prove advantageous for the synthesis of melt-castable explosives or low-melting energetic plasticizers<sup>81</sup>, an area which is currently being explored.

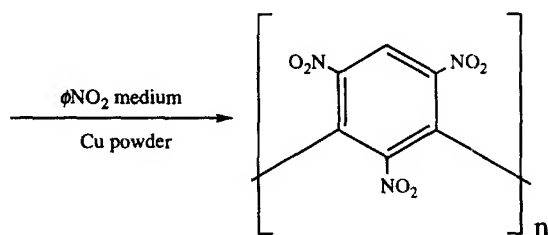
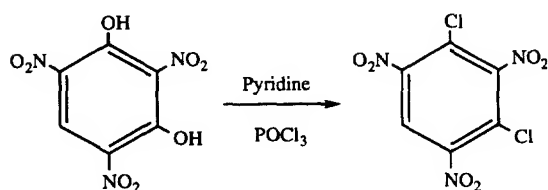
The material in this section is summarized in Table 5.

### 5. ENERGETIC BINDERS FOR EXPLOSIVES AND PROPELLANTS

As mentioned above, the use of inert polymers as binders for explosive formulations brings down the overall energy of such systems. In order to maintain the overall energy of explosive formulations or to improve their performance, the use of energetic or explosive binders has been discussed in the literature. There are some potential binders for this purpose.

#### 5.1. Polynitropolyphenylenes (PNPs)

They describe a class of compounds with aromatic C–NO<sub>2</sub> groups in a chain of benzene units interlinked by aromatic C–C bonds. They may be synthesized by *m*-dichlorotrinitrobenzene (styphnyl chloride) and copper powder in nitrobenzene as a medium, according to Ullmann's reaction<sup>120–122</sup>



(where  $n$  is the degree of polymerization and is in the range 11 to 19).

The structure of this polymeric material has been established on the basis of <sup>1</sup>H-NMR, <sup>13</sup>C-NMR (proves the presence of –C–C– linked aromatic nitrated benzene rings) and molecular weights  $\bar{M}_n$  and  $\bar{M}_w$  by gel permeation chromatography (GPC). The properties are: deflagration temperature 286–294°C, explosion energy 3300 J g<sup>-1</sup>, density 1.8–2.2 g cm<sup>-3</sup>. PNP is of green-brownish yellow to dark brown colour and is soluble in many common solvents. It is insensitive to impact and friction.

PNPs are non-crystalline, exceptionally thermally stable and soluble in common organic solvents, and are considered as high-temperature-resistant binders together with inert binders and/or softeners. Some pyrotechnic formulations that use PNP as a binder have been reported recently<sup>123</sup>.

Owing to recent advances in polymer chemistry, efforts have been made to synthesize polymers containing nitro groups (C–nitro, O–nitro and N–nitro) and the azide group (–N<sub>3</sub>) and use them as binders for explosive/propellant formulations.

A number of energetic polyurethanes based on nitroaliphatic diisocyanates with nitroaliphatic diols have been reported<sup>124</sup>, but none of them has been used as a binder in explosive formulations. C–nitropolymers from monomers with a vinyl group are another class of energetic polymers which may find applications as binders for explosives. Nitroethyl acrylate (CH<sub>2</sub>=CH–COO–CH<sub>2</sub>–CH<sub>2</sub>–NO<sub>2</sub>) monomer, on polymerization under the action of benzoyl peroxide at 100°C in an inert atmosphere, gives a soft polymer, by contrast with the polymer of methacrylate which is hard<sup>125</sup>. The polymer

Table 5. Properties of some melt-castable explosives

Name	Structure/formula	Melting point /°C	Density g/ml	Impact sensitivity/ cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
Tris aziridine melamine (Tris-X)		68-69	1.73	F of I 57	8700	Method of processing similar to TNT using steam
1,3,3, trinitro-azetidine (TNAZ)		101				Steam castable explosive and compatible with explosives and metals
4,4'-dinitro-3,3'-bifurazan		85	1.92	12	8700	Stable up to 254 °C (DTA)

of dinitropropyl acrylate (DNPA) (with a VOD of 6100 m sec<sup>-1</sup>) has also been suggested as a binder for explosive formulations<sup>126</sup>.

### 5.2. Glycidyl Azide Polymer (GAP)

Several groups of researchers have been active in developing glycidyl azide polymer (GAP) for use as an energetic plasticizer as well as an energetic binder. GAP possesses a high density (1.3 g cm<sup>-3</sup>) compared with other polymers used as binders for composite propellants and PBXs, a positive heat of formation (+42 kcal mol<sup>-1</sup>) and the capability to desensitize nitroglycerine (NG), which is an explosive plasticizer and a major ingredient of double-base (DB) and composite-modified double-base (CMDB) rocket propellants. Hence it has been employed both as a plasticizer ( $\bar{M}_n \approx 400-500$ ) as well as a binder ( $\bar{M}_n \approx 3000-3500$ ) in propellants in an effort to enhance specific impulse ( $I_{sp}$ ). A number of publications<sup>127-137</sup> are available in the current literature which deal with almost all aspects of GAP: synthesis, characterization, thermal behaviour, explosive properties and its evaluation in propellant formulations as a plasticizer as well as a binder. The properties of GAP reveal that it may open a new era in the field of explosives in the near future. Based on the analogy of hydroxy-terminated polybutadiene (HTPB), it is speculated that GAP may prove to be a very interesting binder for explosive formulations (PBXs). SNPE, France has already set up a pilot plant for the manufacture of GAP under licence from M/S Rockwell International U.S.A., in order to cater for requirements of European countries<sup>138</sup>.

Some energetic monomers (candidate molecules such as 3,3-(nitratomethyl) methyl oxetane (NIMMO) and

glycidyl nitrate (GLYN)) have also been synthesized by selective nitration with N<sub>2</sub>O<sub>5</sub> followed by their cationic polymerization to the desired molecular weight range and suitable hydroxyl functionality<sup>139</sup>. The OH-terminated molecules may be subsequently crosslinked to give polyurethane rubbers which constitute a new class of energetic rubbers with potential applications in explosives and propellants. Such rubbers are likely to enable variable high-performance and low-vulnerability propellant formulations to be manufactured for the first time<sup>140</sup>.

The strained-ring/N<sub>2</sub>O<sub>5</sub> reactions may also yield energetic plasticizers (starting from nitrogen heterocycles) such as Bu-NENA (O<sub>2</sub>NOCH<sub>2</sub>CH<sub>2</sub>N-NO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), a component of some LOVA propellant formulations<sup>141</sup>.

In addition, the energetic binders that have been reported in the literature are nitrated hydroxy-terminated polybutadiene (nitrated HTPB), poly(3-nitratomethyl-3-methyloxetane) (poly(NIMMO)) and poly(glycidyl nitrate) (poly(GLYN)). Most of the detailed information including their method of synthesis is classified. However, some information is available as follows<sup>142,143</sup>.

### 5.3. Nitrated HTPB

The synthetic route in the early stages involved epoxidation of HTPB in a manner similar to that reported by Zuchowska<sup>144,145</sup> using *in situ* peracetic acid as the epoxidation reagent. Reaction of the epoxide groups with N<sub>2</sub>O<sub>5</sub> in dichloromethane gives a polymer with a percentage of double bonds converted to dinitrate ester groups dependent upon the epoxide content of the intermediate polymer.

Nitrated HTPB with 10% double bonds converted to

Table 6. Some properties of energetic polymeric binders

Polymer	$\bar{M}_n$ (by GPC)	Density (g cm <sup>-3</sup> )	Viscosity (Poise) at 30°C	$T_g$ (°C)
GAP	500–5000	1.3	50	–40
NHTPB	2500	1.20	120	–58
Poly(NIMMO)	2000–15,000	1.26	1350	–25
Poly(GLYN)	1000–3000	1.42	163	–35

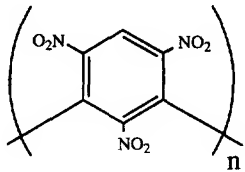
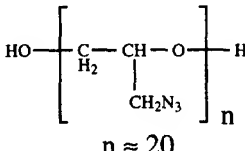
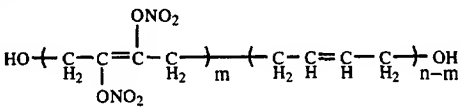
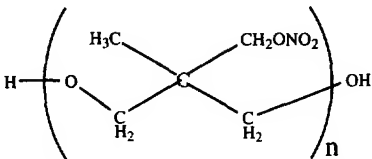
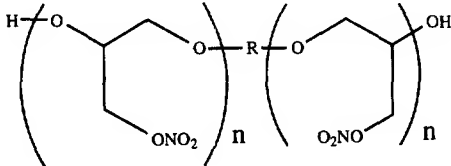
dinitrate ester groups is good for use as a binder. It has viscosity sufficiently low both to make it easy to process and to permit a high solids loading<sup>146</sup>. It can be cured by using aliphatic or aromatic diisocyanates. Its glass transition temperature,  $T_g$ , is, however, slightly higher than that of HTPB but unlike HTPB it has the advantage of being miscible with energetic plasticizers. Its thermal stability is also acceptable. However, large-scale tests have not been performed because poly(NIMMO) and poly(GLYN) have superior performance.

#### 5.4. Poly(NIMMO)

NIMMO is also synthesized by the selective nitration

of the hydroxyl group present in 3-hydroxymethyl-3-methyloxetane (HIMMO) using  $N_2O_5$ . The resulting monomer (NIMMO), on cationic polymerization, yields a pale yellow viscous liquid called poly(NIMMO)<sup>142,143</sup>. This process has been scaled up by the British Defence Research Agency (DRA) and the technology transferred to ICI. The  $T_g$  of the prepolymer (measured by DSC) is –25°C. The thermal stability of the polymer is reasonable (decomposition starts at 170°C). It is now being evaluated as a propellant and explosive binder in large-scale tests. Use of this binder increases the overall energy of a composition and reduces the vulnerability. The DRA has developed a plastic-bonded explosive (PBX) called CPX 413 (based on poly(NIMMO)/HMX/NTO/plastici-

Table 7. Properties of some energetic binders for explosives/propellants

Name	Structure/formula	Melting point /°C	Density g/ml	Impact sensitivity/cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
Polynitro polyphenylenes (PNPs)	 $n \approx 11 \text{ to } 19$	286 to 294	1.8–2.2			Exceptionally thermally stable
Glycidyl azide polymer (GAP)	 $n \approx 20$		1.30	Very insensitive		GAP acts as a plasticizer as well as a binder.
Nitrated hydroxy terminated polybutadiene (NHTPB)			1.2			
Poly(3-nitro-methyl-3-methyl-oxetane) Poly (NIMMO)			1.26	Very insensitive		Hydroxyl terminated Poly (NIMMO) is an energetic binder for rocket propellants, LOVA and PBXs
Poly (glycidyl nitrate) Poly (GLYN)			1.42			Like GAP, it acts as a plasticizer as well as binder

zer) which matches the performance goal of composition B (RDX/TNT 60/40) while passing the UN Series 7 Tests, ranking it as an Extremely Insensitive Detonating Composition<sup>147</sup>.

### 5.5. Poly(GLYN)

Glycidyl nitrate (GLYN) is synthesized in a similar fashion to NINMO by selective -OH nitration of glycidol using  $N_2O_5$ . The yield and purity are both high. GLYN is polymerized into poly(GLYN) by using the same technique used to form poly(NIMMO)<sup>148,149</sup>. However, polymerization of GLYN is more difficult than for NIMMO and is carried out by a different polymerization mechanism. The polymerization is effected by controlling the reaction parameters to induce an active monomer mechanism by using a strong acid initiator such as  $HB F_4$ . A more detailed account of the synthesis and properties of high-molecular-weight poly(GLYN) can be found elsewhere<sup>148</sup>.

Poly(GLYN) is a pale yellow liquid that can be crosslinked with diisocyanates to yield rubbery materials<sup>150</sup>. The polymer imparts high density, high energy and low vulnerability to both propellant and explosive formulations. Its  $T_g$  is  $-35^\circ C$ .

The synthesis of  $\alpha,\omega$ -hydroxy telechelic, low-molecular-weight oligomers (degree of polymerization less than 10) of GLYN and NIMMO by the activated monomer mechanism has also been reported by researchers at DRA Fort Halstead, U.K. The end-nitration of these compounds by dinitrogen pentoxide ( $N_2O_5$ ) in dichloromethane gives  $\alpha,\omega$ -nitrate telechelic oligomers that are envisaged to be energetic and fully compatible (miscible) plasticizers for the new generation of energetic binders such as poly(NIMMO) and poly(GLYN) in propellant and explosive applications<sup>151,152</sup>.

To summarize, the cost of the production of NHTPB is lower than that of poly(NIMMO) or poly(GLYN). However, its performance is poorer. On the basis of trials conducted so far, it seems likely that poly(GLYN) will prove to be a world leader in the field of energetic polymers.

A summary of the properties of energetic binders for use with both explosives and propellants is given in Tables 6 and 7.

## 6. INSENSITIVE HIGH EXPLOSIVES (IHES)

Common explosives like TNT, RDX and HMX used to be considered adequate for all weapon applications, but because of a number of accidents involving initiation of munitions by impact or shock aboard ships, aircraft carriers and ammunition trains, these explosives have become less attractive. So there is much current research world-wide to synthesize explosives that have high performance coupled with low sensitivity.

The conventional, nitrocellulose (NC) and nitroglycerine (NG) based gun propellants are highly prone to accidental initiation as a result of external stimuli (fire, shock wave and impact). The range of threats to gun

ammunition depends on the system in which it is placed. Such threats may be due to shaped charge jets, kinetic energy penetrators, or hot spall. In fact, NC/NG-based propellants are more sensitive than high-explosive warheads, especially when they are stored inside battle tanks or other fighting vehicles. Because of the sensitive nature of NC/NG-based gun propellants, there is always a risk of accidental loss not only of stored ammunition but also of crew members and their vehicles. In order to reduce this risk, LOVA propellants are an attractive alternative for conventional NC/NG-based gun propellants<sup>153-156</sup>.

The problem of warhead vulnerability has become acute in the recent past. The first solution offered to this problem was the invention and use of PBXs, which consist of a polymer matrix encasing a conventional granular explosive, thereby offering some immunity to fire and bullet impact. It was, however, subsequently observed that the use of PBXs alone is no longer sufficient. This problem gave rise to an idea of using an intrinsically less-sensitive explosive. This spawned another class of explosives (thermostable explosive molecules with low-impact sensitivity) termed Insensitive High Explosives (IHEs). TATB is the first member of this class and is considered a reference explosive for invulnerable explosives. TACOT and DINGU are other explosives of this class. It is well known that: (1) HMX is the highest performance explosive for large-scale applications (in terms of VOD and detonation pressure), and (2) TATB is the most invulnerable explosive (in terms of impact sensitivity).

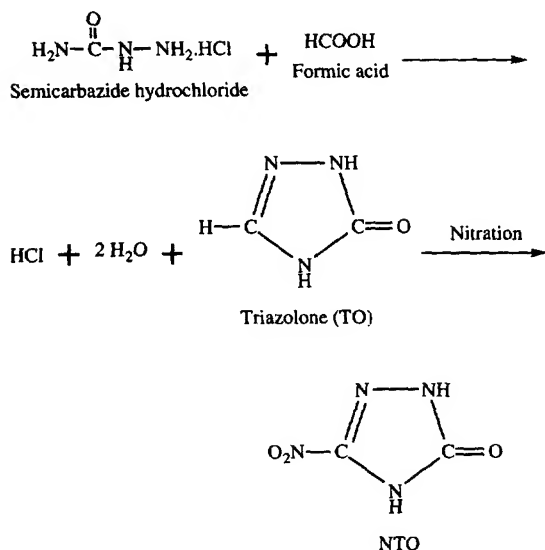
TATB is well-known for its insensitivity and is currently employed as an IHE for some applications. TATB is, unfortunately, inferior to RDX and HMX in performance. Therefore, a need exists for the research and development of explosives that are powerful yet resistant to accidental and sympathetic initiation.

The development of new explosives with increased stability and insensitivity without a decrease in energy, which has been an area of continuous interest and progress in the recent past, is reviewed below.

Norris and co-workers, while working on 5-chloro-4,6-dinitrobenzofuroxan<sup>157</sup>, had an intuition that 7-amino-4,6-dinitrobenzofuroxan (ADNBF) may be an IHE; this was proved to be correct at the end of the investigation<sup>158</sup>. ADNBF is one of the early IHEs equal to TNT in impact sensitivity, with a calculated VOD equal to that of TATB. It is a fairly dense and easily prepared explosive (density  $\approx 1.902 \pm 0.008 \text{ g cm}^{-3}$ , m.p. ca.  $270^\circ C$  (with decomposition), calc. VOD  $\approx 7910 \text{ m sec}^{-1}$ , calc.  $P_{CJ} \approx 28 \text{ GPa}$ , impact sensitivity ( $H_{50\%}$ )  $\approx 53 \text{ cm}$  [TNT =  $54 \text{ cm}$ ], and heat of formation  $\approx +36.79 \pm 0.72 \text{ kcal mol}^{-1}$ ). The work of Norris *et al.* was supported by other researchers who established that the introduction of an  $-NH_2$  group into 4,6-dinitrobenzofuroxan (DNBF) has a remarkable effect upon almost all physical and explosive properties: i.e. m.p., density and calc. VOD all increase significantly, while impact sensitivity is reduced dramatically<sup>159,160</sup>.

### 6.1. Oxynitrotriazole (ONTA) or Nitrotriazolone (NTO)

NTO has been reported as another IHE coupled with better performance<sup>161–166</sup>. Almost all aspects of NTO—synthesis, structural aspects, chemical and explosives properties and thermal behaviour<sup>167–170</sup>—have been investigated. French researchers have recently reported its evaluation as an explosive for warhead filling on its own as well as in a PBX<sup>164</sup>. Furthermore, the synthesis of NTO is easy, consisting of only two steps and uses inexpensive starting materials by the following scheme:



The crystal density of NTO  $\approx 1.93 \text{ g cm}^{-3}$ , and VOD and  $P_C$  are equal to those of RDX. At the same time, it is far less sensitive than RDX and HMX. It is more stable than TNT and RDX, but its sensitivity to ignition is slightly higher than that of TNT. NTO or NTO/RDX or HMX are used as fillings to get insensitive munitions<sup>164</sup>.

A comparison of PBXs based on TATB and NTO further confirms the same sensitivity levels, while the VOD of the NTO-based PBX is slightly higher. The salient feature of NTO as a raw material for PBXs is that it may be obtained in particle sizes much larger than for TATB, i.e. 300–500  $\mu\text{m}$  as against 9–30  $\mu\text{m}$  for TATB, which implies that NTO is suitable for processing by the casting technique also, whereas TATB has to be processed by the coating and pressing technique<sup>164</sup>.

The synthesis and structural characterization of metal salts of NTO, i.e. K, Cu and Pb NTO, reveal that they have special characteristics and may find applications in several fields. The study of their thermal behaviour by DSC suggests that: (1) decomposition of NTO proceeds as a single step; (ii) Cu and K NTO salts decompose in three stages, dehydration, ring breakage and formation of metal oxides; and (3) Pb NTO decomposes in only two steps as it contains no water of crystallization. The structural aspects and thermal decomposition mechanisms of some alkaline earth metal salts of NTO have also been reported, and their mechanisms of decomposition are similar to those mentioned above<sup>171,172</sup>.

American investigators have reported the development of a new IHE called Picatinny Arsenal Explosive-2 (PAX-2, a nitramine-based PBX) which possesses reduced sensitivity to sympathetic detonation in cannon calibre ammunition<sup>173</sup> and is considered a substitute for existing PBXN-5.

### 6.2. Dinitroglycoluril (DINGU)

Some years ago, French scientists reported DINGU as an insensitive explosive, but seemed to lose interest in it subsequently. It is easy to manufacture DINGU (by the nitration of condensation product of glyoxal with urea) at a low cost, which makes it very attractive<sup>174</sup>. On the basis of their studies, Coburn and co-workers termed it an IHE. It is, of course, more sensitive than TATB but much less sensitive than HMX, and is substantially more energetic than TATB<sup>113</sup>. The data of Coburn and co-workers are in agreement with the findings of Chinese workers, who prepared PBXs of DINGU, TNT and RDX using polymer G<sub>505</sub> as a binder and studied VOD, impact and jet sensitivities. The DINGU-based PBXs possess high explosion energy, good physico-chemical stability and outstanding low vulnerability, and are comparable to TATB-based PBXs<sup>175</sup>. As the method of preparation of DINGU is very simple and uses inexpensive starting materials as compared with TATB, the DINGU-based PBXs have a definite edge over TATB-based PBXs.

As discussed in Section 1, the combination of  $-\text{NH}_2$  and  $-\text{NO}_2$  substituent groups provides the inter- and intramolecular hydrogen bonding that stabilizes the molecules and increases the crystal densities. The heterocyclic substrates are included in order to add density compared with the corresponding aromatic analogues and, also in many cases, contribute to a more positive heat of formation. It is with this background that 5-amino-3-nitro-1H-1,2,4-triazole (ANTA) has been tailored and synthesized through three routes<sup>176,177</sup> (the best of which involves the diazotization of 3,5-diaminotriazole followed by reduction with hydrazine).

The structure has been established with the help of IR and NMR. The thermal behaviour and explosive properties—impact, friction and spark sensitivities including VOD—have also been studied. The performance of small-scale tests indicates that ANTA is very insensitive (its impact sensitivity is too low to be determined with a 180 cm impact height limit). This new explosive has been found to be generally insensitive in all sensitivity tests, but of low energy compared with TATB (calculated performance is, however, comparable to that of TATB). ANTA, on treatment with a commercially available compound (4,6-dichloro-5-nitropyrimidine), yields a new IHE which was studied extensively by French workers<sup>178</sup>, but results were not disclosed.

### 6.3. Trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD)

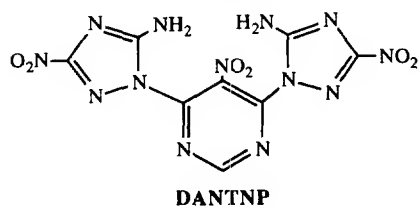
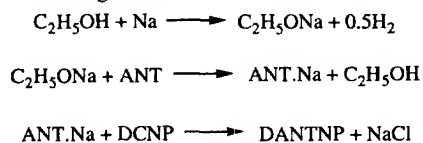
TNAD has been obtained by the reaction of *trans*-1,4,5,8-tetraazadecalin with  $\text{NaNO}_2$  and  $\text{HCl}$  to obtain its

Table 8. Properties of some insensitive high explosives

Name	Structure/formula	Melting point /°C	Density g/ml	Impact sensitivity/ cms	Velocity of detonation (VOD) / m s <sup>-1</sup>	Remarks
7-amino-4,6-dinitro benzofuroxan (ADNBF)		270	1.9	53	7910	Decomposes on melting
5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO)		269	1.93	very insensitive	8510	Can be easily synthesized and is excellent for insensitive ammunitions.
1,4-dinitro glycoluril (DINGU)				Very insensitive		Thermal stability comparable to RDX. Spark and shock sensitivities much less than RDX
3-amino-5-nitro 1H-1,2,4-triazole (ANTA)		244	1.82	>320	8460	Very insensitive to impact, friction and spark
5-nitro-4,6-bis(5-amino-3-nitro-1H-1,2,4-triazole-1-yl)pyrimidine		350	1.86		8200	Impact sensitivity similar to TATB

nitroso derivative followed by its nitration<sup>179</sup>. It has a better thermal stability than RDX and is less sensitive to impact than either RDX or HMX. Its density is equal to that of RDX but its calculated VOD is slightly lower. TNAD is also regarded as an IHE because of its improved insensitivity.

On the basis of their theoretical model, French scientists have tailored an insensitive explosive, 5-nitro-4,6-bis(5-amino-3-nitro-1H-1,2,4-triazole-1-yl)pyrimidine (abbreviated as DANTNP), and synthesized it by the following scheme:



The characteristics of this explosive are: calculated density (X-ray diffraction)  $\approx 1.865 \text{ g cm}^{-3}$ , impact sensitivity (with 5 kg weight)  $\approx 70 \text{ cm}$ , friction sensitivity  $\approx$  insensitive, temperature of decomposition (DSC) *ca.* 350°C and VOD  $\approx 8200 \text{ m sec}^{-1}$ . These confirm that DANTNP is slightly more powerful while its impact insensitivity is of the order of that of TATB<sup>180</sup>.

The material in this section is summarized in Table 8.

Some TNT-based formulations have been tailored, made and tested for sensitivity and ballistic performance. The formulations, which included TATB, DINGU and nitroguanidine, are IHEs and further details are available in the literature<sup>181</sup>.

There are some other interesting explosive compounds, inclusion of which in PBXs improves the insensitivity of the formulations/PBXs. One such compound is 5-hydroxy-3-nitro-1,2,4-triazole (**I**) which has been evaluated in PBXs based on PU and HMX (PU = 19.4, HMX = 21.9 to 80.6 and **I** = 0 to 58.7), and the data show that the sensitivity decreases significantly with increasing proportion of **I**<sup>182</sup>.

## 7. ENERGETIC MATERIALS SYNTHESIZED BY USING NITROGEN PENTOXIDE

It has been the usual practice to synthesize explosives with use of conventional nitrating agents. However, European and American countries have recently moved towards a new nitration methodology based on nitrogen pentoxide or dinitrogen pentoxide ( $N_2O_5$ ). The development and perfection of this new nitration methodology are mainly due to the sustained research in the UK<sup>139</sup>. Nitration with  $N_2O_5$  has several advantages over conventional nitrating agents and may be used to prepare all types of explosives, i.e. C-nitro compounds (TNT, etc.), N-nitro compounds (nitramines like RDX, HMX, etc.) and O-nitro compounds (NG, etc.). Some salient advantages are: (1) it is significantly faster than conventional nitrating agents; (2) yields are higher  $\approx 80$ –90%; (3) purity is of high order; (4) ease of temperature control as reactions are generally non-exothermic; (5) simple product preparation; (6) absence of waste acids for disposal; (7) it is a universal nitrating agent and may be used to prepare all three types of explosive, and is compatible with nitramines.

In fact,  $N_2O_5$  was reported as far back as 1849, but its use was neglected until 1925, mainly because of the difficulty in getting it in pure form and the problems associated with its storage owing to its poor thermal stability<sup>183–185</sup>. It is generally stored at  $-60^\circ\text{C}$  and prepared by: (1) electrolysis of  $HNO_3$  in the presence of  $N_2O_4$ <sup>186</sup>; (2) ozonation of  $N_2O_4$ <sup>187</sup>; (3) dehydration of  $HNO_3$  with  $P_2O_5$ .

It is used for nitration in two ways:

1.  $N_2O_5$  in pure  $HNO_3$ —unselective nitration system akin to a mixed acids system;
2.  $N_2O_5$  in organic solvents—chlorinated solvents encompass a much wider range of nitrations and permit the synthesis of polynitrated species directly without the formation of acidic by-products (an important environmental consideration). It is also suitable for the nitration of strained-ring heterocyclic skeletons.

With the use of this new nitration methodology, Millar and co-workers have reported synthesis of “Tris-X” and its methyl analogue “Methyl Tris-X”<sup>114</sup>. Similarly, French researchers have reported synthesis of 1,3,4,6-tetranitroglycoluril (TNGU or Sorguyl (French)) using  $N_2O_5$ <sup>100</sup>.

Oxidizers and binders are regarded as major ingredients of explosives/propellants and, with the use of  $N_2O_5$  technology, a new series of energetic binders and oxidizers has also been recently reported in the literature. The nitrated hydroxy-terminated polybutadiene (NHTPB), synthesized by selective nitration using  $N_2O_5$  from cheap precursors, is currently undergoing scale-up and evaluation<sup>188</sup>. The initial data suggest its suitability for binder applications<sup>189</sup>. The low-molecular-weight poly(NIMMO) and poly(GLYN) (potential plasticizers) as well as high-molecular-weight poly(NIMMO) and poly(GLYN) (very promising binders) are also manufactured by using  $N_2O_5$ .

The most widely used oxidizer for composite propellants is ammonium perchlorate (AP) which is not environmentally friendly and results in acid rain and the hazard of ozone depletion. Also, its exhaust signature leads to problems of detection and tracking of rockets/missiles<sup>190–194</sup>. There are reports in the literature that AP may be replaced by ammonium dinitramide (ADN), which exhibits high-temperature stability, high energy density and absence of smoke-generating halogens, and thus renders it a useful oxidizer for rocket fuels<sup>195</sup>. Further, its salts are metastable and pumpable oxidizers which may be used in start-stop rocket engines instead of other less stable oxidizers. ADN has also been synthesized with the use of  $N_2O_5$ . The well-known methods of synthesis suitable for scaling up are with  $N_2O_5$  and nitronium tetrafluoroborate ( $NO_2BF_4$ , also made with the help of  $N_2O_5$ )<sup>193,194</sup>.

The material on energetic materials synthesized with the use of  $N_2O_5$  is summarized in Table 9.

Another high-energy and environmentally friendly oxidizer which has recently come to prominence as a result of painstaking research at the European Space Agency (Aerospace Propulsion Products Division) and its sub-contractors (TNO (Delft University of Technology) and the University of Delaware) is hydrazinium nitroformate (HNF), a salt of hydrazine ( $N_2H_4$ ) and nitroform or trinitromethane ( $HC(NO_2)_3$ ). This is made, of course, without the use of  $N_2O_5$ . The most crucial step in the synthesis of HNF is the production of nitroform. The state-of-the-art concerning this oxidizer is that all aspects relating to the practical use of HNF (synthesis, characterization, properties (physical, chemical and explosive), thermal behaviour, toxicity, etc.) have been reported only in the last couple of years<sup>196–203</sup>.

Table 9. Energetic materials synthesized by using nitrogen pentoxide

Name	Structure	Melting point ( $^\circ\text{C}$ )	Density ( $\text{g cm}^{-3}$ )	Remarks
Ammonium dinitramide (ADN)	$NH_4N(NO_2)_2$	92	1.8	More energetic and environment friendly oxidizer
1,3,4,6-Tetranitroglycoluril (TNGU or Sorguyl)	Table 4	—	1.94	
Nitrated hydroxy-terminated polybutadiene (NHTPB)	Table 7	—	1.2	
Tris aziridine melamine (Tris-X)	Table 5	68–69	1.73	
Poly(NIMMO)	Table 7	—	1.26	
Poly(GLYN)	Table 7	—	1.42	

The particle size of HNF crystals is estimated to be between 5 to 10  $\mu\text{m}$ . However, a method has recently been developed to recrystallize HNF to produce particle sizes between 200 and 300  $\mu\text{m}$ . The stability of HNF depends on its purity, and pure HNF has sufficient stability. The European Space Agency has established a production facility for HNF in the Netherlands to produce 100 kg per year. A new propellant based on HNF and glycidyl azide polymer (GAP) binder has recently been reported in Europe. This new propellant containing HNF and GAP promises two new clear advantages:

1. A performance substantially higher (7%) than the best presently known AP/Al/HTPB propellant;
2. Chlorine-free exhaust products.

HNF in conjunction with modern binders like GAP, PGN and poly(NIMMO) not only gives a substantial increase in the performance of solid rocket propellants but also an environmentally benign exhaust as the combustion gases are free from chlorine. The friction and impact sensitivity of HNF/Al/GAP propellants are acceptable and comparable with other propellants and explosives used presently.

Its practical use is primarily hampered by its tendency to attack double bonds in unsaturated binders such as HTPB, causing gas evolution and hence swelling of the propellant. However, the most satisfying characteristic of HNF is its compatibility with the recently reported energetic binders such as GAP, poly(NIMMO) and poly(GLYN).

## 8. TECHNIQUES FOR EXPLOSIVE PROCESSING

A large number of explosives have been reported in recent past. The selection of an explosive is made in the light of stability, reliability, safety, application and mission requirements. At the time of development of a new explosive, it is essential to keep in mind factors such as indigenous availability of the starting materials, ease of the method of preparation, purity of the explosive and its cost-effectiveness, in addition to its impact on the environment.

The technique used to fill an explosive composition into its required casing usually depends on the physical properties of the composition, and so not all techniques are applicable to all types of composition<sup>173,204</sup>. Filling is generally performed through casting, extruding or pressing. The filling process and final integrity of the charge is often critical for the vulnerability of the resulting charge to accidental stimuli. Cracks, micro-pores and debonding from the casing each increase the sensitivity and affect the performance. Melt-cast compositions and certain plastic or thermoplastic compositions can be recast if the quality of the filling is unsatisfactory, but cured PBXs cannot.

The density of the explosive filling contained in munitions should be as close as possible to the theoretical maximum density (TMD) of the compositions. TMD is calculated from the crystal densities of the

components of an explosive composition taking account of their relative proportions.

Depending upon the calibre of the weapon, particle size of the explosive and quantity involved, the processing of an explosive is performed by one of the following techniques.

### 8.1. Melt Casting

RDX/TNT compositions are melt-cast, although the process is not as simple as it sounds. Pure TNT melts at 80.4°C, much lower than its decomposition temperature of 300°C. Therefore it can be safely melted using steam heating. RDX or  $\beta$ -HMX is first incorporated into molten TNT. The viscosity of the filling limits the TNT content to about 75%. This can be increased by casting under vacuum. For some fillings, a small amount of hexanitrostilbene (HNS) is added to the TNT to provide nucleation sites for the TNT. This is very effective in improving the physical integrity and strength of the charge. To ensure that the RDX/TNT fillings do not contain serious flaws, they are X-rayed as a part of quality control.

### 8.2. Casting

PBXs are not melt-cast because the melting points of nitramines are too high to permit steam heating and too close to their decomposition temperatures. However, these materials flow at temperatures between ambient and 100°C and can therefore be cast. Casting is limited by the viscosity of the composition. The upper limit on the explosive content before the material ceases to flow is about 88% by weight. Casting is often performed under vacuum and the filling can be agitated by vibration to dislodge any gas bubbles trapped in the mix. Cast PBXs are cured *in situ*, often at slightly elevated temperatures to reduce the curing time. Once cured, PBXs are dimensionally stable and can be machined if required.

### 8.3. Extrusion

Not all PBXs that are extrudable are produced by extrusion, as some extrude too slowly to be economical. In this process, the composition is mixed and passed directly into the extruder where it is forced through a die of the required size under pressure. This has the obvious economic advantage of allowing the process to be continuous rather than consisting of two batch processes. PBXs that eventually cure should have sufficiently long curing times to prevent curing during this process.

### 8.4. Pressing

PBXs may also be pressed and this method is usually used for the higher explosive content compositions. Pressing is performed by a variety of methods, directly or incrementally with the pressure applied from one direction or with the pressure applied from all directions, hydrostatically or isostatically.



#### 8.4.1. Direct pressing

In this technique, the charge is fabricated with one application of pressure. Vacuum is applied to prevent air from being trapped in the composition during pressing, and densities approaching 99% TMD may be achieved. Direct pressing does, however, lead to a pressing gradient in the material caused by the friction of the composition with the die wall. This adversely affects the performance and sensitivity of the composition.

#### 8.4.2. Incremental pressing

Incremental pressing was developed to overcome the problems associated with direct pressing. In this method, the explosive is not pressed all at one time. Instead, the explosive is added and compacted incrementally until all the material has been pressed to the required density. The increments should be less than the diameter of the charge each time to maximize the effect of this method. Although pressure and density gradients are reduced, they are not eliminated completely by this method and are proportional to the number and size of increments used. In some cases, the interfaces between the increments have been found to cause initiation problems.

#### 8.4.3. Hydrostatic pressing

This technique is used where the charge density and uniformity are critical. The composition is contained in a rubber bag which is evacuated before the application of pressure to the composition by means of an incompressible oil. Although wall friction is eliminated, some residual pressure gradients do occur because the bag rests on a surface at one end.

#### 8.4.4. Isostatic pressing

This technique eliminates almost all the pressure gradient effects found in the other techniques. This is achieved by suspending the rubber bag (containing the material to be pressed) in the fluid so that it is not in contact with any surface while it is being compressed. Isostatic pressing is used for high-performance fillings where densities greater than 99% TMD are required. It is, however, relatively slow and expensive compared with the other methods and is only now just being developed for wider use in PBX production.

Pressed compositions can also be machined if required afterwards but this is carried out remotely because of the hazards involved.

An explosive consisting of fine particles will not have a uniform coating of binder. Furthermore, if it is processed by the casting technique, the explosive loading is poor, resulting in poor performance. High explosive loading is possible with an explosive consisting of a multimodal particle size distribution. Crystal size and crystal perfection of an explosive are likely to affect many factors such as decomposition, deflagration, deflagration-to-detonation transition (DDT), strength,

sensitivity, etc. Research on crystal size, morphology, perfection, defects, etc. are the key factors in the optimization of explosives in the future.

Experience with explosives such as DATB, TATB, PYX, etc. suggests that the synthesis of explosives with coarse particles may prove to be a real bottleneck and no ready-made solutions to this problem are available as there are no standard methods available to increase particle size. The parameters reported<sup>205</sup> to affect particle size are: (1) concentrations of the precipitating solutions; (2) temperatures of the precipitating solutions; (3) rate of cooling of the solutions<sup>165</sup>; (4) material of construction of the stirrer, (5) rotation rate of the stirrer. By varying one parameter at a time, the effect of each of them on particle size can be determined and hence ways may be found to increase the particle size of an explosive. However, this requires an in-depth study.

## 9. CONCLUSIONS

From this review in the field of high-energy materials, it clearly emerges that the high-energy explosive hexanitrohexaazaisowurtzitane (HNIW or CL-20), the melt-castable explosive trinitroazetidine (TNAZ), the insensitive high explosive nitrotriazolone (NTO), the energetic binders for composite and LOVA propellants and PBXs poly(3-nitratomethyl-3-methyloxetane) (poly(NIMMO)) and poly(glycidyl nitrate) (poly(GLYN)), and the environmentally friendly oxidizer for rocket propellants, ammonium dinitramide (ADN), are all very interesting materials, holding very promising potential for large-scale production and use. However, their cost of production is very high and is thus a limiting factor in their use at present. Therefore, effort needs to put into making their production cost-effective. In view of the advantages of  $N_2O_5$  technology over the conventional nitrating agents (as well as its good environmental properties), this synthesis method is likely to be used more and more widely for production of high-energy materials in future.

Another area that needs immediate attention is the synthesis of high-energy materials with large particle size to make them suitable for processing with the casting technique at higher solids loading.

*Acknowledgements*—The author is grateful to the European Commission for the award of a Marie Curie Fellowship, and to Dr Haridwar Singh, Director of the High Energy Materials Research Laboratory (Pune, India) for arranging study leave. The author would like to express his sincere thanks to Professor J. E. Field and Drs P. M. Dickson and S. M. Walley for comments upon this manuscript and for help with its preparation.

## REFERENCES

1. Davis T. L., *The Chemistry of Powder and Explosives*, Vol. 2. John Wiley, New York (1943).
2. Cook M. A., *The Science of High Explosives*, Reinhold, New York (1958).

3. Urbanski T., *Chemistry and Technology of Explosives* (3 vols), Pergamon, Oxford (1964).
4. Bailey, A. and Murray S. G., *Explosives, Propellants and Pyrotechnics*, Brassey's, Oxford (1989).
5. Urbanski T., *Chemistry and Technology of Explosives*, Vol. 4, Pergamon, Oxford, p. 202 (1984).
6. Dunstan, I., Chemistry in the technology of explosives and propellants. *Chemistry in Britain*, 1971, 7, 62–69.
7. Urbanski, T. and Vasudeva, S. K., Heat-resistant explosives. *J. Sci. Ind. Res.*, 1978, 37, 250–255.
8. Lu, C. X., Development and present situation of heat resistant explosives. *Kogyo Kayaku*, 1990, 51, 275–279.
9. Gilbert, E. E. and Sollott, G. P., Explosive compound undergoes testing. *Chem. and Engng News*, 1980, 58, 32.
10. Gilbert, E. E., The preparation of hexanitrobiphenyl from TNT with sodium hypochlorite. *Propell. Explos.*, 1980, 5, 15–19.
11. Iyer, S., Explosive desensitisation studies via chemical group modification of nitroso-derivatives of RDX and 3-amino-TNT. *Propell. Explos. Pyrotech.*, 1982, 7, 37–39.
12. Iyer, S., Explosive desensitization studies via chemical group modification. II: 3,5-diamino- and 3,5-dichloro-2,4,6-trinitrotoluene. *J. Energ. Mater.*, 1984, 2, 151–158.
13. Hutchinson, C. D., Mohan, V. K. and Millar, R. W., Aminotriptyl: synthesis, spectral characterisation, thermal decomposition and explosive properties. *Propell. Explos. Pyrotech.*, 1984, 9, 161–171.
14. Ayres, J. N., Montesi, L. J. and Bauer, R. J., Small scale gap test data compilation, Vol. 1. Report No. NOLTR 73-132 (1973).
15. Gibbs, T. R. and Popolato, A., *LASL Explosive Property Data*. Univ. California Press, Los Angeles, p. 38, 157 (1980).
16. Meyer, R., *Explosives*. Verlag Chemie, Weinheim (1981).
17. Zeman, S., The thermoanalytical study of some amino derivatives of 1,3,5-trinitrobenzene. *Thermochim. Acta*, 1993, 216, 157–168.
18. Ott, D. G. and Benziger, T. M., Preparation of 1,3,5-triamino-2,4,6-trinitrobenzene from 3,5-dichloroanisole. *J. Energ. Mater.*, 1987, 5, 343–354.
19. Chaykovsky, M. and Adolph, H. G., Synthesis and properties of some trisubstituted trinitrobenzenes: TATB analogues. *J. Energ. Mater.*, 1990, 8, 392–414.
20. Wright, S. B., Granular explosive molding powder. US Patent No. 3173817 (1965); *Chem. Abstr.*, 1965, 62, 12968g.
21. Wright, S. B., Granulated crystalline plastic-bonded explosives. US Patent No. 3296041 (1967); *Chem. Abstr.*, 1967, 66, 87227p.
22. Bailey, A., Bellerby, J. M. and Kinloch, S. A., The identification of bonding agents for TATB/HTPB polymer bonded explosives. *Phil. Trans. R. Soc. Lond.*, 1992, A339, 321–333.
23. Kaye, S. M., *Encyclopedia of Explosives and Related Items*, Vol. 9. ARDEC, Dover, NJ, pp. T34–T55 (1980).
24. Jackson, R. K. and Weingart, R. C., Detonation properties of the insensitive explosive TATB. *Chem. Abstr.*, 1976, 85, 179841.
25. Jackson, R. K. and Weingart, R. C., Detonation properties of the insensitive explosive TATB. *Chem. Abstr.*, 1977, 86, 45331.
26. Kolb, J. R. and Rizzo, H. F., Growth of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). I: Anisotropic thermal expansion. *Propell. Explos.*, 1979, 4, 10–16. (and references therein).
27. Rosen, J. M. and Dacons, J. C., The relationship of thermal stability with structure of some trinitrophenyl explosives. *Explosivstoffe*, 1968, 16, 250–252.
28. Lu, C. X., Lu, Z. S. and Deng, A. M., Research on condensation reaction in synthesis in potassium 3,3'-diamino-2,2',4,4',6,6'-hexanitro diphenyl amide. *Chem. Abstr.*, 1991, 115, 32128g.
29. Coburn, M. D. and Jackson, T. E., Picrylamino substituted heterocycles. III: 1,2,4-triazoles. *J. Heterocycl. Chem.*, 1968, 5, 199–203.
30. Coburn, M. D., 3-picrylamino-1,2,4-triazole. US Patent No. 3483211 (1969); *Chem. Abstr.*, 1970, 72, 55458x.
31. Li, J., Chen, B. and Ou, Y., Modified preparation and nitration of 3-picrylamino-1,2,4-triazole. In *Proc. 17th Int. Pyrotech. Seminar (combined with the 2nd Beijing Inst. Symp. on Pyrotechnics and Explosives)*, Vol. 1. Beijing Inst. Tech. Press, Beijing, pp. 196–199 (1991).
32. Shipp, K. G., Reactions of substituted polynitrotoluenes. I: Synthesis of 2,2',4,4',6,6'-hexanitrostilbene. *J. Org. Chem.*, 1964, 29, 2620–2623.
33. Shipp, K. G. and Kaplan, L. A., Reactions of substituted polynitrotoluenes. II: The generation and reactions of 2,4,6-trinitrobenzyl anion. *J. Org. Chem.*, 1966, 31, 857–861.
34. Golding, P. and Hayes, G. F., Studies on the synthesis of 2,2',4,4',6,6'-hexanitrostilbene. *Propell. Explos.*, 1979, 4, 115–120.
35. Bement, L. J., Application of temperature resistant explosives to NASA missions. In *Proc. Symp. on Thermally Stable Explosives*, Whiteoak, MD. Naval Ordnance Laboratory (1970).
36. O'Keefe, D. M., Hexanitrotetrachloroazobenzene explosive and method of preparation. U.S. Patent No. 4751289 (1988); *Chem. Abstr.*, 1988, 109, 152561r.
37. Hasman, E., Gvishi, M. and Carmel, Y., Measurement of shock initiation threshold of HNAB by flyer plate impact. *Propell. Explos. Pyrotech.*, 1986, 11, 144–149.
38. Feng, Z.-G. and Chen, B.-R., Synthesis of 3,3'-bis(2,2',4,4',6,6'-hexanitrostilbene). *Propell. Explos. Pyrotech.*, 1991, 16, 12–15.
39. Chen, B. and Feng, Z., Synthesis of 2,2',4,4',6,6'-hexanitro-3-methylnitro aminostilbene. *Chem. Abstr.*, 1987, 107, 117877k.
40. Urbanski T., *Chemistry and Technology of Explosives*, Vol. 4. Pergamon, Oxford, p. 206 (1984).
41. Coburn, M. D., Picrylamino-substituted heterocycles. I: 2,4,6-tris(picrylamino)-s-triazine and related compounds. *J. Heterocycl. Chem.*, 1966, 3, 365–366.
42. Coburn, M. D. and Singleton, J. L., Picrylamino-substituted heterocycles. V: Pyridines. *J. Heterocycl. Chem.*, 1972, 9, 1039–1044.
43. Harris, B. W., Singleton, J. L. and Coburn, M. D., Picrylamino-substituted heterocycles. VI: Pyrimidines. *J. Heterocycl. Chem.*, 1973, 10, 167–171.
44. Baytos, J. F., Los Alamos National Laboratory Report No. LA-5829-MS (1975).
45. Riggs, R. S., Explosive 1,3,5-trinitro-2,4,6-tripicryl benzene. US Patent No. 2904544 (1960); *Chem. Abstr.*, 1960, 54, 11062.
46. Riggs, R. S., Explosive 1,3,5-trinitro-2,4,6-tripicryl benzene. U.S. Pat. No. 4861924 (1989); *Chem. Abstr.*, 1990, 112, 59246u.
47. Carboni, R. A., Dibenzotetraazacyclooctatetraene and derivatives. US Patent No. 2904544 (1959); *Chem. Abstr.*, 1960, 54, 11062d.
48. Carboni, R. A. and Castle, J. E., Dibenzotetraazapentalene: a new heteroaromatic system. *J. Am. Chem. Soc.*, 1962, 84, 2453–2454.
49. Harder, R. J., Carboni, R. A. and Castle, J. E., Aromatic azapentalenes. V: 1,1'- and 2,2'-bibenzotriazoles and their conversion to dibenzotetraazapentalenes. *J. Am. Chem. Soc.*, 1967, 89, 2643–2647.
50. Coburn, M. D., 2,6-Bis(picrylamino)-3,5-dinitropyridine and a method for its preparation. U.S. Patent No. 3678061 (1972).
51. Pallanck, R. G., PYX purification. U.S. Patent No. 4564405 (1986); *Chem. Abstr.*, 1986, 104, 209534n.
52. Sitzmann, M. E., 2,5-Dipicryl-1,3,4-oxadiazole: a shock sensitive explosive with high thermal stability (thermally stable substitute for PETN). *J. Energ. Mater.*, 1988, 6, 129–144.

53. Kamlet, M. J. and Adolph, H. G., The relationship of impact sensitivity with structure of organic high explosives. II: Polynitro aromatic explosives. *Propell. Explos.*, 1979, **4**, 30–34.
54. Kaye, S. M., *Encyclopedia of Explosives*, Vol. 8. ARDEC, Dover, NJ, p. N169 (1978).
55. Dacons, J. C., Nonanitroterphenyl. U.S. Patent No. 3 755 471 (1973); *Chem. Abstr.*, 1974, **80**, 49964h.
56. Gilbert, E. E., Thermally stable octanitro macrocyclic explosives. U.S. Patent No. 3 941 812 (1976); *Chem. Abstr.*, 1976, **85**, 23292r.
57. Ritter, H. and Wanders, B., Polynitropyridine: a new class of explosives. *Chem. Abstr.*, 1988, **113**, 81640k.
58. Buckley, E., Everard, J. E. and Wells, C. H. J., Synthesis of 1,3,5- and 1,4,5-trinitro- and 1,3,5,7- and 1,3,5,8-tetranitro-2,6-dimethyl naphthalene. *Chemistry and Industry (London)*, 1978, **124**, 124–125.
59. Buckley, E., Houellebecq, T. F. and Wells, C. H. J., Synthesis of 2,4,8- and 4,5,8-trinitro- and 2,4,5,7- and 2,4,5,8-tetranitro-1-methyl naphthalene. *Chemistry and Industry (London)*, 1981, **127**, 774–775.
60. Avrami, L., in *Encyclopedia of Explosives and Related Items*, Vol. 9, eds. S. M. Kaye and H. L. Herman. ARDEC, Dover, NJ, pp. R5–R67 (1980).
61. Bowden, F. P. and Yoffe, A. D., *Initiation and Growth of Explosion in Liquids and Solids*. Cambridge University Press (1952) (republ. 1985).
62. Mellor, A. M., Boggs, T. L., Covino, J., Dickinson, C. W., Dreitzler, D., Thorn, L. B., Frey, R. B., Gibson, P. W., Roe, W. E., Kirshenbaum, M. and Mann, D. M., Hazard initiation in solid rocket and gun propellants and explosives. *Prog. Energy Combust. Sci.*, 1988, **14**, 213–244.
63. Walley, S. M., Field, J. E. and Palmer, S. J. P., Impact sensitivity of propellants. *Proc. R. Soc. Lond.*, 1992, **A438**, 571–583.
64. Field, J. E., Bourne, N. K., Palmer, S. J. P. and Walley, S. M., Hot spot ignition mechanisms for explosives and propellants. *Phil. Trans. R. Soc. Lond.*, 1992, **A339**, 269–283.
65. Dickson, P. M. and Field, J. E., Initiation and propagation in primary explosives. *Proc. R. Soc. Lond.*, 1993, **A441**, 359–375.
66. Coffey, C. S. and de Vost, V. F., Impact testing of explosives and propellants. *Propell. Explos. Pyrotech.*, 1995, **20**, 105–115.
67. Bonnett, D. L. and Butler, P. B., Hot-spot ignition of condensed phase energetic materials. *J. Propulsion Power*, 1996, **12**, 680–690.
68. Chapman, D. L., On the rate of explosion in gases. *Philos. Mag. (Ser. 5)*, 1899, **47**, 90–104.
69. Jouguet, E., Sur la propagation des réactions chimiques dans les gaz: avant propos; hypothèses et équations fondamentales; les ondes ordinaires. *J. Math. Pures Appliquées (6<sup>ème</sup> Sér.)*, 1905, **1**, 347–425.
70. Jouguet, E., Sur la propagation des réactions chimiques dans les gaz: les ondes de choc. *J. Math. Pures Appliquées (6<sup>ème</sup> Sér.)*, 1906, **2**, 5–86.
71. Bliss, D. E., Christian, S. L. and Wilson, W. S., Impact sensitivity of polynitroaromatics. *J. Energ. Mater.*, 1991, **9**, 319–345.
72. Vanderah, D. J., A parametric study of the synthesis of 2,3,4,6-tetranitroaniline. *J. Energ. Mater.*, 1990, **8**, 391–392.
73. Gasco, A. and Boulton, A. J., Furoxans and benzofuroxans. In *Advances in Heterocyclic Chemistry*, Vol. 29, ed. A. R. Katritzky. University of Florida Press (1991).
74. Wang, N-X., Chen, B-R. and Ou, Y-X., Synthesis of N,N'-bis(2,4-dinitrobenzofuroxan)-1,3,5-trinitro-2,6-diaminobenzene. *Propell. Explos. Pyrotech.*, 1993, **18**, 111–112.
75. Hudson, F. M., Synthesis of 2,6-bis(picrylamino)-3,5-dinitropyridine. Eur. Pat. Appl. EPO 104717 (1984); *Chem. Abstr.*, 1984, **101**, 110736f.
76. Chen, B. and Liao, Z., Synthesis of 5,7-diamino-4,6-dinitrobenzofuroxan. In *Proc. 21st Int. Ann. Conf. ICT*, Fraunhofer Institut für Chemische Technologie, Karlsruhe, Germany, paper 58 (1990).
77. Chafin, A. P. and Atkins, R. L., Method for preparing explosive compounds. US Patent No. 4 754 040 (1988); *Chem. Abstr.*, 1989, **110**, 10723s.
78. Wang, N., Chen, B. and Ou, Y., Synthesis of N,N'-bis(2-nitrobenzodifuroxanyl)-3,5-dinitro-2,6-diamino pyridine. *J. Energ. Mater.*, 1993, **11**, 47–50.
79. Wang, N-X., Chen, B-R. and Ou, Y-X., Review on benzofuroxan system compounds. *Propell. Explos. Pyrotech.*, 1994, **19**, 145–148.
80. Yinon, J. and Read, R. W., MS/MS of energetic compounds. A collision induced dissociation (CID) study of some polynitrobiphenyl-2-amines. *J. Energ. Mater.*, 1991, **9**, 191–204.
81. Sitzmann, M. E., Gilligan, W. H., Ornellas, D. L. and Trasher, J. S., Polynitroaliphatic explosives containing pentafluorosulfonyl (SF<sub>5</sub>) group: the selection and study of a model compound. *J. Energ. Mater.*, 1990, **8**, 352–374.
82. Hudlicky, M., *Chemistry of Organic Fluorine Compounds*, 2nd edn. Halstead Press, New York, Ch. 7 (1976).
83. Kamlet, M. J. and Jacobs, S. J., Chemistry of detonations. I: A simple method for calculating detonation properties of C–H–N–O explosives. *J. Chem. Phys.*, 1968, **48**, 23–25.
84. Marchand, A. P., Synthesis and chemistry of novel polynitro polycyclic cage molecules. *Tetrahedron*, 1988, **44**, 2377–2395.
85. Marchand, A. P., Annapurna, P., Arney Jr., B. E., Dave, P. R., Gadgil, V. R., Rajapaksa, D., Sharma, G. V. M., Sharma, R. and Zope, U. R., Synthesis and explosive performance characteristics of polynitro polycyclic cage explosives. In *Proc. 4th Int. Symposium on Anal. Detect. Explos.*, The Weizmann Institute of Science, Jerusalem, pp. 241–263 (1992).
86. Marchand, A. P., Synthesis and chemistry of homocubanes, bishomocubanes and trishomocubanes. *Chem. Rev.*, 1989, **89**, 1011–1033.
87. Marchand, A. P. and Suri, S. C., Synthesis of 3,5,5-trinitropentacyclo[5.3.0.0.0.0.0]decane. *J. Org. Chem.*, 1984, **49**, 2041–2043.
88. Marchand, A. P., Sharma, G. V. M., Annapurna, G. S. and Pednekar, P. R., Synthesis of pentacyclo[5.4.0.0.0.0.0]undecane-4,8,11-trione-(D<sub>3</sub>-trishomocubane-1,2,3-trione) and 4,4,7,7,11,11-hexanitro[6.3.0.0.0.0.0]undecane-(D<sub>3</sub>-hexanitrotrishomocubane). *J. Org. Chem.*, 1987, **52**, 4784–4788.
89. Marchand, A. P., Dave, P. R., Rajapaksa, D. and Arney Jr., B. E., Synthesis of 4,4,8,8,11,11-hexanitropentacyclo[5.4.0.0.0.0.0]undecane. *J. Org. Chem.*, 1989, **54**, 1769–1771.
90. Su, Z., Guan, X. and Yu, Y., Synthesis of the pentacyclo-[4.3.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]nonane-2,4-bis(trinitroethyl ester). In *Proc. 17th Int. Pyrotech. Seminar (combined with the 2nd Beijing Int. Symp. on Pyrotechnics and Explosives)*. Beijing Inst. Tech. Press, Beijing, pp. 224–228 (1991).
91. Sollott, G. P., Alster, J., Gilbert, E. E., Sandus, O. and Slagg, N., Research towards novel energetic materials. *J. Energ. Mater.*, 1986, **4**, 5–28.
92. Eaton, P. E. and Shankar, B. K. R., Synthesis of 1,4-dinitrocubane. *J. Org. Chem.*, 1984, **49**, 185–186.
93. Griffin, G. W., Umrigar, P. P. and Vaz, C. J., *Working Group Meeting on Synthesis of High Density Energetic Materials*. ARDEC, Dover, NJ (1984).
94. Zajac, W. W., Manufacture of multinitrated caged molecules for explosives. US Pat. No. 5 105 031 (1992); *Chem. Abstr.*, 1992, **117**, 114729j.
95. Marchand, A. P., Synthesis of new high energy/high density monomers and polymers: synthesis of D<sub>3</sub>-hexanitrotrishomocubane. In *Proc. Naval Workshop on Energetic Crystalline Materials*. Office of Naval Research, MD (1986).
96. Iyer, S., Damavarapu, R., Strauss, B., Bracuti, A., Alster,

- J. and Stec, D. III, New high energy density materials for propellant applications. *J. Ballistics*, 1992, **11**, 72–79.
97. Neilsen, A. T., Nissan, R. A., Vanderah, D. J., Coon, C. L., Gilardi, R. D., George, C. F. and Flippen-Anderson, J., Polyazapolycyclics by condensation of aldehydes with amines. 2: Formation of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0<sup>3,9</sup>.0<sup>3,11</sup>]dodecanes from glyoxal and benzylamines. *J. Org. Chem.*, 1990, **55**, 1459–1466.
  98. Crampton, M. R., Hamid, J., Millar, R. and Ferguson, G., Studies of the synthesis, protonation and decomposition of 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0<sup>3,9</sup>.0<sup>3,11</sup>]dodecane (HBIW). *J. Chem. Soc. Perkin Trans. II*, 1993, 923–929.
  99. Wardle, R. B., Hinshaw, J. C., Braithwaite, P., Johnstone, G., Jones, R., Poush, K., Lyon, V. A. and Collignon, S., Development of the caged nitramine hexanitrohexaazaisowurtzitane. In *Proc. International Symposium on Energetic Materials Technology*. American Defence Preparedness Association (1994).
  100. Boileau, J., Emeury, J. M. L. and Kehren, J. P., Tetranitroglycoluril for explosives. US Patent No. 4 487 938 (1974); *Chem. Abstr.*, 1985, **83**, 30483r.
  101. Oyumi, Y. and Brill, T. B., Thermal decomposition. XXVIII: Predictions and results for nitramines of bis-imidazolidinedione: DINGU, TINGU and TDCD. *Propell. Explos. Pyrotech.*, 1988, **13**, 69–73.
  102. Hong, G. and Zhu, C., Synthesis and properties of tetranitropropanediurea. In *Proc. 17th Int. Pyrotech. Seminar (combined with the 2nd Beijing Int. Symp. on Pyrotechnics and Explosives)*. Beijing Inst. Tech. Press, Beijing, pp. 193–195 (1991).
  103. Boileau, J., Piteau, M. and Jacob, G., Synthèse de la 1,3,5,5-tetranitrohexahydropyrimidine. *Propell. Explos. Pyrotech.*, 1990, **15**, 38–40.
  104. Levins, D. A., Cichra, D. A. and Adolph, H. G., Nitrolysis of dialkyl tert-butylamines. *J. Org. Chem.*, 1982, **47**, 2472–2476.
  105. Levins, D. A., Jose, S., Bedford, C. D. and Coon, C. L., Synthesis of 1,3,5,5-tetranitrohexahydropyrimidine (DNNC). US Patent No. 4 346 222 (1982); *Chem. Abstr.*, 1983, **98**, 18971a.
  106. Shackelford, S. A. and Goldman, J. F., Heat of fusion of DNNC and its DNNC-d<sub>6</sub> deuterium labelled analogue. *Propell. Explos. Pyrotech.*, 1995, **20**, 1–4.
  107. Licht, H. H. and Ritter, H., Neue Sprengstoffe: Ihre Leistung in Theorie und Experiment. In *Proc. 21st ICT Int. Annual Conf.* Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 9 (1990).
  108. Zeng, M. and Lang, H., A study of synthesis and thermal stabilities of 2,4,6-trinitropyridine and its derivatives. In *Proc. 1st Symp. on Pyrotechnics and Explosives*. Beijing, China Academic Publishers (1987).
  109. Licht, H. H. and Ritter, H., 2,4,6-Trinitropyridine and related compounds: synthesis and characterization. *Propell. Explos. Pyrotech.*, 1988, **13**, 25–29.
  110. Ritter, H. and Licht, H. H., Synthesis and characterisation of methylnitramino-substituted pyridines and triazines. *Propell. Explos. Pyrotech.*, 1993, **18**, 81–88.
  111. De Fusco, A. A. and Neilson, A. T., Diaminotetranitronaphthalene for use as a high energy high density explosive. U.S. Patent No. 4 531 013 (1985); *Chem. Abstr.*, 1986, **104**, 21512z.
  112. Hu, R., Lu, X. and Fang, Y., Thermal behaviour of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaaza-tricyclo[7.3.0.0]dodecane-5,11-dione. *J. Energ. Mater.*, 1993, **11**, 219–241.
  113. Coburn, M. D., Harris, B. W., Lee, K. Y., Stinecipher, M. M. and Hayden, H. H., Explosives synthesis at Los Alamos. *Ind. Engng. Chem. Prod. Res. Dev.*, 1986, **25**, 68–72.
  114. Millar, R. W., Paul, N. C., Richards, D. H., Bunyan, P., Golding, P. and Rowley, J. A., Tris-X, a new high energy polynitramine explosive: synthesis using dinitrogen pentoxide technology, characterization, and thermal stability and hazard assessment. *Propell. Explos. Pyrotech.*, 1993, **18**, 55–61.
  115. Archibald, T. G., Gilardi, R., Baum, K. and George, C., Synthesis and X-ray crystal structure of 1,3,3-trinitroazetidine. *J. Org. Chem.*, 1990, **55**, 2920–2924.
  116. Iyer, S., Velicky, R., Sandus, O. and Alster, J., Research toward more powerful explosives. Technical Report No. ARAED-TR-89010, ARDEC, Picatinny Arsenal (1989).
  117. Doali, J. O., Fifer, R. A., Kruczynski, D. I. and Nelson, B. J., The Mobile Combustion Diagnostic Fixture and its application to the study of propellant combustion. Part I: Investigation of the low pressure combustion of LOVA XM-39 propellant. Technical Report No. BRL-MR-378/5, US Ballistic Research Laboratory, MD (1989).
  118. Coburn, M. D., Picrylamino substituted heterocycles. II: Furazans. *J. Heterocycl. Chem.*, 1968, **5**, 83–87.
  119. Coburn M. D., N<sup>2</sup>, N<sup>4</sup>, N<sup>6</sup>-tripicrylmelamine, an explosive. US Patent No. 3 414 570 (1968); *Chem. Abstr.*, 1969, **70**, 47505d.
  120. Fanta, P. E., The Ullmann synthesis of biaryls. *Chem. Rev.*, 1946, **38**, 139–196.
  121. Fanta, P. E., The synthesis of biaryls, 1945–1963. *Chem. Rev.*, 1964, **64**, 613–632.
  122. Redecker, K. H. and Hagel, R., Polynitropolyphenylenes: a high temperature resistant, non-crystalline explosive. *Propell. Explos. Pyrotech.*, 1987, **12**, 196–201.
  123. Berger, B., Haas, B. and Reinhard, G., Einfluss des Bindergehaltes auf das Reaktionsverhalten Pyrotechnischer Mischungen. In *Proc. 26th Int. Arm. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 2 (1995).
  124. Herman, H. L., Nitropolymers. In *Encyclopedia of Explosives*, Vol. 8, ed. S. M. Kaye. ARDEC, Dover, NJ, pp. N138–N157 (1978).
  125. Marans, N. S. and Zelinski, R. P., Nitroalkyl esters of acrylic, crotonic and methacrylic acids. *J. Am. Chem. Soc.*, 1950, **72**, 2125–2129.
  126. Ville, J., Sur quelques dérivés du nitroforme. *Mém. Poudres*, 1960, **42**, 21–27.
  127. Frankel, M. B. and Flanagan, J. E., Azido polymer with terminal hydroxyl groups. Belgian Patent No. 89 858 (1979).
  128. Frankel, M. D. and Flanagan, J. E., Azido polymer with terminal hydroxy groups. US Patent No. 4 268 450 (1980); *Chem. Abstr.*, 1980, **93**, 47806c.
  129. Wagner, R. I., Wilson, E. R., Grant, L. R. and Flanagan, J. E., GAP polymer binder for propellants and its preparation. U.S. Patent No. 4 937 361 (1981).
  130. Ahad, E., Branched hydroxy terminated azido aliphatic polyethers. US Patent No. 4 882 395 (1989); *Chem. Abstr.*, 1990, **112**, 159265t.
  131. Ahad, E., Process for the preparation of alkyl azide substituted hydroxy terminated polyethers. U.S. Patent No. 4 891 438 (1990); *Chem. Abstr.*, 1988, **109**, 17114Ou.
  132. Mama, H. P., Solid rocket propellants: the European scene. *Int. Def. Rev.*, 1990, **21**, 291–295.
  133. Frankel, M. B., Grant, L. R. and Flanagan, J. E., Historical development of GAP. *J. Propulsion Power*, 1992, **8**, 560–563.
  134. Kubota, N., Sonobe, T., Yamamoto, A. and Shimizu, J., Burning rate characteristics of GAP propellants. *J. Propulsion Power*, 1990, **6**, 686–689.
  135. Nazare, A. N., Asthana, S. N. and Singh, H., GAP—an energetic component of advanced solid rocket propellants—a review. *J. Energ. Mater.*, 1992, **10**, 43–63.
  136. Schedlbauer, F., LOVA gun propellants with GAP binder. *Propell. Explos. Pyrotech.*, 1992, **17**, 164–171.
  137. Dhar, S. S., Asthana, S. N., Singh, S. and Nata, G. N., Thermal decomposition of GAP and GAP based double-base propellants. *Combust. Explos. Shock Waves*, 1993, **29**, 276–280.

138. Schoyer, H. E. R. and Schnorhk, A. J., A new solid propellant: good possibilities. *European Space Agency's Preparing for the Future*, 1992, **2**, 3–5.
139. Millar, R. W., Colclough, M. E., Golding, P., Honey, P. J., Paul, N. C., Sanderson, A. J. and Stewart, M. J., New synthesis routes for energetic materials using dinitrogen pentoxide. *Phil. Trans. R. Soc. Lond.*, 1992, **A339**, 305–319.
140. Debenham, D., Leeming, W. B. H. and Marshall, E. J., New energetic formulations containing nitropolyethers. In *Proc. Joint Int. Symp. on Compatibility of Plastics*, Arlington, VA. American Defence Preparedness Association (1991).
141. Olsen, R. E., Fisch, D. W. and Hamel, E. E., Nitrations by nitronium tetrafluoroborate. In *Advanced Propellant Chemistry (Advanced Chemistry Series No. 54)*, ed. R. E. Gould. American Chemistry Society, Washington, D.C., Ch. 6 (1966).
142. Colclough, M. E., Desai, H., Millar, R. W., Paul, N. C., Stewart, M. J. and Golding, P., Energetic polymers in composite propellants and explosives. *Polym. Adv. Technol.*, 1994, **5**, 554–560.
143. Colclough, M. E., Paul, N. C., Desai, H. and Shepherd, N., DRA approaches to new energetic binders. *J. Ballistics*, 1995, **12**, 169–176.
144. Zuchowska, D., Polybutadiene modified by epoxidation. 1: Effect of polybutadiene microstructure on the reactivity of double bonds. *Polymer*, 1980, **21**, 514–520.
145. Zuchowska, D., Polybutadiene modified by epoxidation: 2. The effect of epoxy groups on the crosslinking process with dicumyl peroxide. *Polymer*, 1981, **22**, 1073–1075.
146. Colclough, M. E. and Paul, N. C., Nitrated hydroxy-terminated polybutadiene: synthesis and properties. *Am. Chem. Soc. Symp. Ser.*, 1996, **623**, 97–103.
147. Cumming, A. S., Characteristics of novel United Kingdom energetic materials. In *Proc. Int. Symp. on Energetic Materials Technology*. American Defence Preparedness Association, pp. 68–74 (1995).
148. Desai, H. J., Cunliffe, A. V., Lewis, T., Millar, R. W., Paul, N. C., Stewart, M. J. and Amass, A. J., Synthesis and properties of high molecular weight poly(GLYN). *Polymer*, in press.
149. Cheun, Y.-G., Cho, J. R. and Kim, J. S., An improved synthetic method of poly(NIMMO) and PGN prepolymer. In *Proc. Int. Symp. on Energetic Materials Technology*. American Defence Preparedness Association, pp. 61–67 (1995).
150. Leeming, W. B. H., Marshall, E. J., Bull, H., Rodgers, M. J. and Paul, N. C., An investigation into poly(GLYN) cure stability. In *Proc. 27th Int. Ann. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 99 (1996).
151. Desai, H. J., Cunliffe, A. V., Hamid, J., Honey, P. J., Stewart, M. J. and Amass, A. J., Synthesis and characterization of ( $\alpha,\omega$ -hydroxy and nitrate telechelic oligomers of 3,3-(nitratomethyl) methyl oxetane (NIMMO) and glycidyl nitrate (GLYN). *Polymer*, 1996, **37**, 3461–3469.
152. Desai, H. J., Cunliffe, A. V., Lewis, T., Millar, R. W., Paul, N. C., Stewart, M. J. and Amass, A. J., Synthesis of narrow molecular weight ( $\alpha,\omega$ -hydroxy telechelic poly-(glycidyl nitrate) and estimation of theoretical heat of explosion. *Polymer*, 1996, **37**, 3461–3476.
153. Juhasz, A. A. and Rocchio, J. J., Combustion properties of LOVA propellants. In *Proc. 13th Int. Arm. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, pp. 545–561 (1982).
154. Wise, S. and Law, H., The low-vulnerability ammunition programme. *Army Res. Develop. Acquisition Mag.*, 22–23 (Sept.–Oct. 1983).
155. Wise, S. and Rocchio, J. J., A development process for low vulnerability propellants. In *Proc. 13th Int. Ann. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, pp. 539–544 (1982).
156. Mezger, M., Strauss, B., Moy, S., Prezelski, J. and Lu, P., The development of insensitive explosives. In *Proc. Joint Int. Symp. on Compatibility of Plastics and other Materials with Explosives, Propellants, Pyrotechnics and Processing of Explosives, Propellants and Ingredients*. American Defence Preparedness Association, pp. 2–8 (1988).
157. Norris, W. P. and Chafin, A., Synthesis and thermal rearrangement of 5-chloro-4,6-dinitrobenzofuroxan. *Heterocycles*, 1984, **22**, 271–274.
158. Norris, W. P., 7-Amino-4,6-dinitrobenzofuroxan: an insensitive high explosive. Report No. NWC TP-6522, Naval Weapons Center, China Lake, CA (1984).
159. Rothstein, L. R. and Petersen, R., Predicting high explosive detonation velocities from their composition and structure. *Propell. Explos.*, 1979, **4**, 56–60.
160. Hobin, T. P., Some aminodinitro derivatives of benzofurazan and benzofurazan oxide. *Tetrahedron*, 1968, **24**, 6145–6148.
161. Bugaut, F., Bernard, S. and Chirat, R., Theoretical prediction of high explosives efficiency: application to NTO. In *Proc. 9th Symp. (Int.) on Detonation*. Office of the Chief of Naval Research, Arlington, VA, pp. 489–497 (1989).
162. Becuwe, A. and Delclos, A., Use of oxynitrotriazole to prepare an insensitive high explosive. In *Proc. 9th (Int.) Symp. on Detonation*. Office of the Chief of Naval Research, Arlington, VA, pp. 1008–1013 (1989).
163. Lee, K.-Y., Chapman, L. B. and Coburn, M. D., 3-Nitro-1,2,4-triazol-5-one: a less sensitive explosive. *J. Energ. Mater.*, 1987, **5**, 27–33.
164. Becuwe, A. and Delclos, A., Low-sensitivity explosive compounds for low vulnerability warheads. *Propell. Explos. Pyrotech.*, 1993, **18**, 1–10.
165. Collignon, S. L., Preparation of spheroidal 3-nitro-1,2,4-triazole-5-one. US Patent Appl. US 213037 (1989); *Chem. Abstr.*, 1989, **110**, 234222r.
166. Gimenez, P., Chabin, P., Mala, J. and Spyckerelle, C., An extensive experimental study of pressed NTO. In *Proc. 10th (Int.) Symp. on Detonation*, ed. J. M. Short and D. G. Tasker. Office of Naval Research, Arlington, VA, pp. 493–497 (1995).
167. Ostmark, H., The chemistry of 3-nitro-1,2,4-triazole-5-one (NTO) thermal decomposition. *Thermochim. Acta*, 1993, **213**, 165–175.
168. Beard, B. C., Early decomposition chemistry of NTO. In *Proc. 10th (Int.) Symp. on Detonation*, ed. J. M. Short and D. G. Tasker. Office of Naval Research, Arlington, VA, pp. 204–207 (1995).
169. Rothgery, E. F., Audette, D. E., Wedlich, R. C. and Csejka, D. A., The study of the thermal decomposition of NTO by DSC, TGA-MS, and ARC. *Thermochim. Acta*, 1991, **185**, 235–243.
170. Ciller, J. A., Serna, F. and Quintana, J. R., Thermal characterisation of mixtures of nitrotriazolone with HMX and RDX. *J. Energ. Mater.*, 1992, **10**, 251–265.
171. Xie, Y., Hu, R.-Z., Wang, X.-Y. and Fu, X.-Y., Thermal behaviour of 3-nitro-1,2,4-triazole-5-one (NTO) and its salts. In *Proc. 17th International Pyrotech. Seminar (combined with the 2nd Beijing Int. Symp. on Pyrotechnics and Explosives)*, Vol. 1. Beijing Inst. Tech. Press, Beijing, pp. 509–514 (1991).
172. Zhang, T., Hu, R. and Li, F., Structural characterization and thermal decomposition mechanisms of alkaline earth metal (Mg, Ca, Sr, and Ba) salts of 3-nitro-1,2,4-triazole-5-one. *Thermochim. Acta*, 1994, **244**, 185–194.
173. Manning, T., Strauss, B., Mezger, M. and Jamison, C., Processing evaluation of new insensitive explosives. *J. Ballistics*, 1992, **11**, 45–52.
174. Boileau, J., Carail, M., Wimmer, E., Gallo, R. and Pierrot, M., Dérives nitrés acétylés du glycoluril. *Propell. Explos. Pyrotech.*, 1985, **10**, 118–120.

175. Li, J., The LOVA composite explosives containing DINGU. In *17th Int. Pyrotech. Seminar (combined with 2nd Beijing Int. Symp. on Pyrotechnics and Explosives)*. Beijing Inst. Tech. Press, Beijing, pp. 322–332 (1991).
176. Lee, K. Y., Storm, C. B., Hiskey, M. A. and Coburn, M. D., An improved synthesis of 5-amino-3-nitro-1H-1,2,4-triazole (ANTA): a useful intermediate for the preparation of insensitive high explosives. *J. Energ. Mater.*, 1991, **9**, 415–428.
177. Simpson, R. L., Pagoria, P. F., Mitchell, A. R. and Coon, C. L., Synthesis, properties and performance of the high explosive ANTA. *Propell. Explos. Pyrotech.*, 1994, **19**, 174–179.
178. Laval, F., Wartenberg, C. and Morignat, M. L., 5-Nitro-4,6-bis-[(5-nitro-1H-1,2,4-triazolyl)amino] pyrimidine. Process for its preparation and explosive material containing it. Eur. Pat. Appl. EP 320370 (1989); FR Appl. 87/17059 (1987); *Chem. Abstr.*, 1989, **111**, 194786q.
179. Willer, R. L., Trans-1,4,5,8-tetranitro-1,4,5,8-tetra azadecaline. U.S. Patent No. 4443 602 (1984); *Chem. Abstr.*, 1984, **101**, 72759f.
180. Wartenberg, C., Charrue, P. and Laval, F., Conception, synthèses et caractérisation d'un nouvel explosif insensible et énergétique: le DANTNP. *Propell. Explos. Pyrotech.*, 1995, **20**, 23–26.
181. Licht, H. H., Performance of castable IHE formulations. *Chem. Abstr.*, 1989, **111**, 236138n.
182. Becuwe, A. and Delclos, A., L'oxynitrotriazole et son utilisation en tant qu'explosif insensible. In *Proc. 18th Int. Arm. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 27 (1987).
183. Deville, M. H., Note sur la production de l'acide nitrique anhydre. *C.r. hebdomadaire Séances Acad. Sci. Paris*, 1849, **28**, 257–260.
184. Haines, L. B. and Adkins, H., The reaction of certain organic compounds with nitrogen pentoxide. *J. Am. Chem. Soc.*, 1925, **47**, 1419–1426.
185. Addison, C. C. and Logan, N., in *Developments in Inorganic Nitrogen Chemistry*, ed. C. B. Colburn. Elsevier, Amsterdam, Ch. 2 (1973).
186. Harrar, J. E. and Pearson, R. K., Electrosynthesis of  $N_2O_3$  by controlled potential oxidation of  $N_2O_4$  in anhydrous  $HNO_3$ . *J. Electrochem. Soc.*, 1983, **130**, 108–112.
187. Harris, A. D., Trebellas, J. C. and Jonassen, H. B., Vanadium (V) oxide nitrate and chromium (VI) oxide nitrate. *Inorg. Synth.*, 1967, **9**, 83–88.
188. Colclough, M. E., Golding, P. and Paul, N., Nitrated hydroxy terminated polybutadiene (NHTPB): a new energetic binder. In *Proc. 14th Int. Pyrotech. Semin.* Henry Ling Press, Dorset, UK, pp. 105–111 (1989).
189. Stewart, M., Arber, A., Bragg, G., Colclough, E., Desai, H., Millar, R., Paul, N. and Salter, D., Novel energetic monomers and polymers prepared using  $N_2O_5$  chemistry. In *Proc. 21st Int. Ann. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 3 (1990).
190. Rossi, M. J., Bottaro, J. C. and McMillen, D. F., The thermal decomposition of the new energetic material, ammonium dinitramide in relation to nitramide and ammonium nitrate. *J. Chem. Kinetics*, 1993, **25**, 549–570.
191. Brill, T. B., Brush, P. J. and Patil, D. G., Thermal decomposition of energetic materials. 58: Chemistry of ammonium nitrate and ammonium dinitramide near the burning surface temperature. *Combust. Flame*, 1993, **92**, 178–186.
192. Mebel, A. M., Lin, M. C. and Morokuma, K., Theoretical study of the gas-phase structure, thermochemistry, and decomposition mechanisms of  $NH_4NO_2$  and  $NH_4N(NO_2)_2$ . *J. Phys. Chem.*, 1995, **99**, 6842–6848.
193. Bottaro, J. C., Schmitt, R. J., Penwell, P. E. and Ross, D. S., Dinitramide salts and method of making same. US Patent Appl. PCT/US91/04268 (1991); Int. Publ. no. WO91/19669; *Chem. Abstr.*, 1992, **116**, 217513t.
194. Bottaro, J. C., Schmitt, R. J., Penwell, P. E. and Ross, D. S., Method of forming dinitramide salts. US Pat. Appl. PCT/US91/04277 (1991); Int. Publ. No. WO91/19670; *Chem. Abstr.*, 1992, **116**, 217512s.
195. Bottaro, J. C. Recent advances in explosives and solid propellants. *Chem. Indust.*, 249–252 (1 April 1996).
196. Schmidt, E. W., *Hydrazine and its Derivatives: Preparation, Properties and Applications*. Wiley, New York (1984).
197. Zee, F. W. M., Mul, J. M. and Hordijk, A. C., Method of preparing hydrazine nitroform. Int. Patent Application No. PCT/NL-93/00230, The Netherlands (1993).
198. Hordijk, A. C., Mul, J. M., Meulenbrugge, J. J., Korting, P. A. O. G., van Lit, P. J., Schnorhk, A. J. and Schöyer, H. F. R., Properties of hydrazine nitroformate: a new oxidiser for high performance solid propellants. In *Proc. 25th Int. Ann. Conf. ICT*. Fraunhofer Institut für Chemische Technologie, Karlsruhe, paper 69 (1994).
199. Mul, J. M., Korting, P. A. O. G. and Schöyer, H. F. R., A search for new storable high-performance propellants. *ESA Journal*, 1990, **14**, 253–270.
200. Mul, J. M., Gadiot, G. M. H. J. L., Meulenbrugge, J. J., Korting, P. A. O. G., Schnorhk, A. J. and Schöyer, H. F. R., New solid propellants based on energetic binders and hydrazinium nitroformate. *Acta Astronautica*, 1993, **29**, 771–779.
201. Schöyer, H. F. R., Schnorhk, A. J., Korting, P. A. O. G., van Lit, P. J., Mul, J. M., Gadiot, G. M. H. J. L. and Meulenbrugge, J. J., High performance propellants based on HNF. *J. Propulsion Power*, 1995, **11**, 856–869.
202. Schöyer, H. F. R., ESA's new solid propellant based on hydrazinium nitroformate. *ESA's Preparing for the Future*, 1996, **6**, 6–7.
203. Williams, G. K. and Brill, T. B., Thermal decomposition of energetic materials. 67: Hydrazinium nitroformate (HNF) rates and pathways under combustionlike conditions. *Combust. Flame*, 1995, **102**, 418–426.
204. Johnson, N. C., Gotzmer, C. and Gill, R. C., Melt cast elastomeric PBXs: processing and properties overview. *J. Hazard. Mater.*, 1984, **9**, 41–45.
205. Pennie, A. M. The preparation of a crystalline high explosive of controlled particle size by precipitation with water from acetone solution. *Canad. J. Chem. Engng*, 78–81 (April 1958).